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TRACER MEASUREMENT OF STREAM REAERATION

E. C. Tsivoglou

Federal Water Pollution Control Administration
Washington, D.C.

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Tracer Measurement of Stream Reaeration

by

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tracer measurement of stream reaeration introduction

The purpose of this report is to present an entirely new method for the direct and independent field determination of the reaeration capacity of natural flowing streams. The technique involves the use of a radioactive gaseous tracer for oxygen, and this report contains detailed descriptions of the technique, its basis, the supporting laboratory investigations and the full-scale field demonstration. The tracer technique makes possible a new and direct approach to the problem of evaluating stream self-purification capacity and waste treatment requirements, with a degree of accuracy and dependability not heretofore achievable. In any specific instance, the costs of waste treatment are inversely related to the reaeration capacity of the receiving stream, and, without definite information regarding the reaeration capacity, it has not been possible to predict the costs of pollution abatement programs with an adequate degree of accuracy. Thus, the new tracer method for measuring reaeration has important implications regarding the full success of current nationwide efforts to improve stream water quality and to plan for the most efficient use of the nation's water resources.

The ability of a flowing stream to obtain oxygen from the limitless resources of the atmosphere is the fundamental process by which the stream is able to "purify itself" once it has been polluted with organic wastes. Without this "reaeration capacity," a stream degraded by oxygen-depleting wastes could never recover its dissolved oxygen resources. It would remain degraded forever, and the great variety of aquatic life that we take for granted could not exist. Yet, to date, the reaeration capacity of a natural stream has never been independently and accurately measured, although attempts to evaluate the real process date back at least half a century.

There is good reason why the independent measurement of stream reaeration capacity in the natural situation has been so difficult to accomplish. Oxygen transfer from the atmosphere can take place only at the air-water interface that exists at the stream surface, and this interface is constantly and randomly changing, or being renewed, due to turbulent mixing of the flowing water. Unfortunately, turbulence is a very complex process, and is not susceptible to independent measurement or evaluation. We therefore have no independent means of knowing the rate with which new volume elements of water reach the surface, or the rate of surface renewal. The most obvious approach to determining reaeration capacity, the direct one based upon evaluation of turbulence, therefore cannot be used. As a result,

it has been necessary over the years to attempt to evaluate reaeration of natural streams on the basis of an indirect method.

The primary stream self-purification processes, which always take place, are the depletion of dissolved oxygen resources due to bacterial degradation of dissolved organic pollution, and replenishment of the oxygen resources by absorption of oxygen from the atmosphere, or reaeration. Other natural stream processes, superimposed, that may significantly modify dissolved oxygen concentration include the oxygen demands of organic river bottom deposits, or sludge, and the photosynthetic and respiratory activities of algae, and the activities of bacterial slime that grow on the stream bed. Stream self-purification refers to the net effect of these and other less significant processes, all occurring simultaneously, on the stream oxygen resources.

The traditional indirect method of Streeter and Phelps for estimating stream reaeration consists of calculating the reaeration that must have taken place in a specific stream reach by attempting to evaluate the effects of all of the other natural stream processes that have modified dissolved oxygen concentration, and then basing the calculation on a theoretical equation for stream self-purification. Such an approach presumes, in the first place, that the theoretical model for self-purification is, in fact, quite correct, and, secondly, that we can independently and accurately evaluate the dissolved oxygen effects of all of the other stream processes. Although this indirect approach is rational, it cannot yield accurate estimates of stream reaeration capacity in any except the most ideal and simple situations, because the actual stream self-purification process is more complex than the mathematical models that are available, and also because available knowledge regarding certain of the individual natural processes that modify dissolved oxygen concentration is quite limited and incomplete. Thus, the traditional indirect approach to estimating stream reaeration capacity has required assumptions that cannot be verified, and the calculations involve a circular argument that can and does result in gross error. Although it has been the only available rational attack, the indirect method has therefore also failed to provide a means of knowing stream reaeration capacity without doubt.

Accurate knowledge of stream reaeration capacity is a principal key to successful pollution control and abatement. It is the necessary basis for accurate determination of waste treatment requirements in any specific situation, and is thereby the principal requirement for accurate evaluation of the costs of pollution control. A single example will serve to illustrate the direct importance of knowing reaeration capacity: Recent extensive studies of waste treatment needed to maintain a specific minimum dissolved oxygen objective in the waters of a major eastern river basin have indicated that the capital costs of waste treatment facilities will range in that case from about $50 to $200 million, depending upon the actual reaeration capacity. This wide range of estimated costs could not be narrowed further because the reaeration capacity could not be determined more definitely. The range of estimated annual operating costs was similarly affected by the indeterminacy of reaeration capacity. Planning for pollution control can hardly be expected to be really effective unless the costs can be more definitely known.

Because of its crucial importance in determining waste treatment requirements and associated costs, accurate and dependable evaluation of the reaeration capacity is also the only rational basis for sound judgment regarding the real suitability of proposed dissolved oxygen standards, in the practical sense that the proposed standard may be too high to be technically feasible or economically reasonable, or too low in terms of the stream quality improvement that could reasonably be expected, or quite appropriate in terms of technical feasibility and associated costs.

The gaseous tracer method described here permits direct and independent evaluation of stream reaeration capacity. It constitutes a direct measurement of gas exchange capacity in a specific stream reach under existing hydrodynamic conditions, and does not depend upon idealized theoretical constructions that cannot be verified. Application of this measuring technique is not limited to presently polluted stream reaches, as is the case for the traditional indirect approach. On the contrary, as the tracer method really measures the effects of turbulence and surface renewal on gas exchange, it can be applied in any river reach, before pollution occurs as well as after, and its usefulness is not affected by the presence or absence of sludge deposits, algae, zero dissolved oxygen levels, or other similar conditions. The ability to accurately evaluate reaeration capacity in presently unpolluted river reaches should prove to be especially advantageous in selecting sites and planning for pollution control for new industry, as well as in basinwide water quality and water resources planning.

basic considerations and historical background

This chapter contains a general qualitative discussion of the gas exchange process in turbulent water systems and an outline of the currently available procedures for estimating natural stream reaeration capacity. These discussions are limited to the concepts and the material that pertain directly to the subject of the report. It is emphasized that the gaseous tracer method for the direct measurement of the reaeration capacity of natural streams does not depend for validity upon these qualitative descriptions of the gas transfer process.

CHAPTER ONE

BASIC CONSIDERATIONS

Reaeration of turbulent water is a purely physical process that takes place as the result of the combined effects of the molecular diffusion of oxygen and the physical mixing of the water. Diffusion of the gas through the air-water interface, and subsequently within the fluid medium, is the basic process at work, but the mixing associated with turbulence greatly enhances the gas diffusion process and thereby hastens reaeration. The following discussions regarding the separate effects of molecular diffusion and mixing are intended only to serve as the brief qualitative descriptions necessary for understanding the whole gas exchange process. Therefore no attempt has been made to make these discussions comprehensive or fully general, especially in the mathematical sense. For more extensive discussions and the related detailed mathematical developments regarding molecular diffusion and turbulent mixing, the reader is referred to the various sources cited in the following sections of the report.

Gas Transfer in Turbulent Water

Reaeration of oxygen-deficient water involves both the ability of the oxygen molecules to enter the water from the overlying atmosphere and their tendency subsequently to diffuse within the liquid medium. If the water is being mixed or stirred, the gas process is more rapid. It is important to distinguish carefully between the processes of molecular diffusion and mixing, or dispersion, for purposes of studying stream reaeration. *Diffusion* refers to the movement of molecules from a region of higher to a region of lower concentration as a result of the inherent kinetic energy possessed by the molecules themselves. *Dispersion,* on the other hand, causes the transfer of volume elements of fluid (and therefore of the gas molecules contained in the volume elements) due to the application of the external forces associated with the directional motion of the fluid. Taken alone, molecular diffusion is a slow process, whereas the addition of dispersion, or mixing, greatly hastens gas transfer within the fluid.

For purposes of the following discussion, a volume element of water is taken to be large enough to contain a great number of dissolved gas molecules, but is a very small portion of fluid. A very large number of volume elements is required to be a sample, no matter how small the sample.

Molecular Diffusion.—Consider a hypothetical beaker of water that is absolutely still—no fluid

motion of any kind occurs. The beaker is open to the atmosphere, and the water is initially devoid of oxygen. The oxygen molecules that are present in the overlying atmosphere possess an inherent average kinetic energy associated with the prevailing temperature, and may be visualized as tiny projectiles, darting about at random and colliding with each other as well as with other molecules that are present. In contrast to the main body of fluid, the water molecules in the surface layer are arrayed in a quite orderly fashion, as a result of the unbalanced forces of molecular attraction at the surface. The water surface (a few molecules thick) can therefore be thought of as containing an orderly array of holes or spaces that gas molecules can enter, and as having the appearance of a screen, or grid, to an oncoming gas molecule. The immediate water surface thus represents a barrier that must be crossed before a gas molecule can become a part of the main body of fluid.

A small fraction of the oxygen molecules in the overlying atmosphere that are near the air-water interface happen to move toward the fluid surface, some of these penetrate the water surface and enter the fluid medium. They become molecules of dissolved oxygen, and the concentration of oxygen molecules in the uppermost water layers increases with time. The rate at which the gas molecules enter the fluid is proportional to the gas pressure above the water surface, and if the gas pressure remains constant (as it does in the case of stream reaeration), the rate of entry of gas molecules is constant.

The dissolved gas molecules also move about in random directions within the fluid medium, due to their inherent kinetic energy. Of the oxygen molecules present in the uppermost water layers after a short time, a fraction will chance to move upward, and some of these will penetrate the surface and escape back into the overlying atmosphere. Similarly, other oxygen molecules from the uppermost fluid layers will happen to move downward. At any moment the concentration of gas molecules in the uppermost water layers is greater than the concentration in the neighboring deeper layers, and the random motion of all of the gas molecules therefore results in a larger number moving downward. This tends to reduce the dissolved oxygen concentration in the uppermost water layers. On the other hand, the number of gas molecules that escapes back into the atmosphere is proportional to the concentration of gas molecules in the uppermost water layers, and in the early period of the experiment the rate of escape to the atmosphere is therefore small compared to the constant rate of entry from the atmosphere. This tends to increase the dissolved oxygen concentration in the uppermost water layers. As a result of these influences, the net transfer of the oxygen molecules is always downward through the fluid medium, and the concentration of oxygen molecules in the uppermost water layers is continually replenished from the overlying atmosphere.

At any moment in time after the beginning of the experiment, the concentration of dissolved oxygen is therefore a continuous function of liquid depth, and the deeper the point of observation, the lower the oxygen concentration. From a different point of view, if the dissolved oxygen concentration were observed at a single depth over a period of time, it would be seen to increase in a smooth, continuous fashion as time passed.

In the completely still system that has been postulated, at any moment in time the difference in concentration of oxygen molecules between neighboring layers of water within the main body of fluid will be infinitesimally small. Therefore, almost as many oxygen molecules will move upward from the deeper layer as will move downward from the upper water layer. The net rate of gas transfer downward through the liquid can thus only be very slow, and it is clear that if reaeration depended only upon the molecular diffusion of oxygen in still water, it would be a very slow process.

Eventually, after quite a long time, if molecular diffusion is the only force at work, the entire body of water will achieve a uniform concentration of oxygen molecules, and there will be no further variation of dissolved oxygen with liquid depth. When this point has been reached, the rate of escape of gas molecules from the uppermost water layer to the atmosphere will just equal the constant rate of entry of gas molecules from the atmosphere into the water. An equilibrium is thus eventually achieved and this condition is referred to as dissolved oxygen saturation. Other conditions remaining constant, there will be no further change of oxygen concentration within the fluid medium.

Dispersion.—Suppose now that instead of the postulated, completely still fluid system, some mixing or circulatory motion is imparted to the volume elements of water by the application of an external force. (Whether this motion is the

result of recirculation of the water, the use of a mechanical stirrer, or the presence of temperature differentials within the fluid medium, is immaterial.) Volume elements of water now circulate freely throughout the fluid medium, and for present purposes their movement relative to each other can be regarded as essentially random in nature. Volume elements from the deeper regions of the fluid replace some of those at the surface, and the latter move into the deeper main body of fluid. Some of the liquid volume elements from the uppermost water layers suddenly find themselves immediately adjacent to volume elements that an instant earlier were located quite deep in the beaker. The latter contain relatively little dissolved oxygen, whereas the volume elements from the surface layers contain a high concentration. The gas concentration difference between these neighboring volume elements of water is thus no longer infinitesimal, but is quite large; and the net rate of movement of gas molecules from the richer to the poorer volume elements is therefore relatively rapid. At the same time, volume elements from the deeper regions of the beaker appear briefly at the surface and as they are relatively poor in terms of dissolved oxygen content, take up oxygen from the atmosphere at a relatively rapid rate.

At any instant there is a wide distribution of "ages" of all of the individual volume elements of water in a turbulent fluid system, in terms of the period of time that has passed since they were at the interface. The range of "ages" is conceptually from zero (at the interface) to infinity (never having been at the interface). The individual volume elements therefore possess an infinity of concentrations of oxygen molecules, ranging up to the saturation concentration. Similarly, the individual volume elements of water that make up the surface water layer at any moment possess a wide range of "ages," ranging from zero (just arrived at the surface) to infinity (never having been away from the surface), and associated oxygen concentrations ranging up to saturation. The typical volume element of water moves up from the deeper regions of the fluid and appears briefly at the surface, where it absorbs additional oxygen from the atmosphere; it then moves back down into the deeper regions, where it gives up some of its oxygen molecules to other volume elements that contain a lower concentration because they have not visited the surface so recently. The typical (average) volume element of water will be exposed at the surface for a definite and limited period of time, even though the individual volume elements remain at the surface for a wide range of times and contain a wide range of oxygen concentrations. (Obviously, the volume elements of water do not retain an individual identity for any finite period of time, and the foregoing qualitative description of gas transfer is oversimplified in that sense. Also, any real sample contains a very large number of volume elements of water, and so the observable oxygen concentration in a well-mixed system will be uniform throughout at any moment.)

In a turbulent water system such as a flowing stream, the transfer of oxygen from the atmosphere into the water therefore takes place in two steps. The gas molecules must first enter the fluid medium from the atmosphere by penetrating the surface water layer, which consists of an orderly array of water molecules and constitutes a barrier that must be overcome. After entering the fluid medium, the oxygen molecules are transferred by diffusion, and the rate of diffusion within the main body of water is a direct function of the oxygen concentration difference between neighboring layers or volume elements of water. Within the hypothetical absolutely still water this difference is everywhere infinitesimal, and the gas transfer process within the fluid proceeds very slowly. Mixing or dispersion of the volume elements of water aids the gas transfer process in two ways: It results in "renewal" of the surface water layer, in the sense that surface volume elements of water are replaced steadily by others from the deeper regions that contain less oxygen, and this results in a larger net rate of transfer at the interface; secondly, mixing increases the oxygen molecule concentration difference between neighboring volume elements of water within the main body of fluid, and this hastens diffusion within the fluid medium. The degree to which mixing hastens gas transfer is thus a direct function of the rate of mixing, or the rate with which the volume elements of water are moved about.

The distinction between true molecular diffusion and dispersion, or mixing, is thus quite clear. Even a very slight degree of mixing of the water layers will substantially increase the net rate of gas transfer over that due solely to molecular diffusion, and violent mixing of the type associated with a rapid turbulent stream will result in a relatively very rapid gas transfer process. Unfortunately, the literature on turbulence and on reaeration of streams does not distinguish clearly between diffusion and dispersion, but confuses

these terms. In particular, the term "diffusion" has been widely used to refer to mixing processes, in expressions such as "hydrodiffusion," "eddy diffusion" and "turbulent diffusion." It is therefore emphasized that, throughout this report, the term "diffusion" refers only to the molecular process described earlier, and has nothing to do with the hydrodynamic properties of fluids in motion. These hydrodynamic properties of the fluid relate to dispersion, and although this hastens diffusion, it is an entirely separate process subject to different laws.

The foregoing qualitative description of gas transfer in a turbulent or mixed water system leads directly to the well-known conclusion that the rate of change of the saturation deficit is proportional to the deficit at any time, and that the saturation deficit is the driving force for gas transfer. Introduction of the concepts and procedures of the classical kinetic theory of gases [1] and of physical chemistry [2] permits conversion to a quantitative basis. Conversion from the molecular to the macroscopic scale of reference and to gas pressures is provided by consideration of the properties of large numbers of gas molecules according to the kinetic theory. Following the procedures of physical chemistry, the concept of "activity" rather than concentration of gas molecules may be introduced, and the driving force for gas transfer becomes the difference in "chemical potential." All of the well-known gas laws are thus shown to apply to the air-water system under consideration, including Henry's Law, Dalton's law of partial pressures and the ideal gas law.

This discussion has referred primarily to the transfer of oxygen and to the process known as reaeration in natural waters. However, the same principles apply directly to the transfer of other gases as well and, as will be seen, the only significant difference between the transfer capabilities of different gases is associated with the molecular properties of the gases. These principles apply also regardless of the direction of gas transfer, or whether the net movement of the gas is into or out of the water.

Turbulence

For the sake of simplicity, the foregoing description of gas transfer in a turbulent water system assumed perfect mixing, in the sense that the system was taken to be everywhere homogeneous at all times. This convenient view in no way discredits the qualitative description of the gas transfer process, but it does incorporate certain implied assumptions that prevent its direct quantitative application to some real situations. The assumption of perfect mixing implies a steady mixing rate and a steady rate of replacement of the surface volume elements by those from the deeper fluid regions, as well as uniformity of mean dissolved gas concentration throughout the fluid. It implies also that the surface volume elements of water are freely replaced by others from below, without unusual difficulty, and that no shearing stresses exist between fluid layers anywhere. In essence, the description presumed ideal mixing of an ideal fluid, as well as transfer of an ideal gas. Such assumptions, while quite useful for qualitative descriptive purposes, are not usually valid for real experimental systems, and are especially hazardous in regard to natural stream flow conditions.

As has been seen, mixing sharply enhances and hastens the diffusion process, and in a mixed water system the actual rate of gas transfer depends primarily upon the kind and degree of mixing and turbulence. Fluid turbulence is perhaps most suitably regarded as a departure from laminar flow, and in a perfectly mixed system it is characterized by the random occurrence of eddies that vary over a wide range of frequency, amplitude, and direction. In an imperfectly mixed system, for instance, one having a stable vortex, the associated eddies are not fully random so far as direction, frequency, and amplitude are concerned. Real situations usually involve imperfect mixing in one way or another. In particular, at a free water surface the water molecules tend to orient themselves with relation to each other in such a way as to create a quite orderly molecular array at the air-water interface. The water has surface tension, and the uppermost layers have a tendency to slide over, rather than to mix freely, with the deeper fluid layers. A shearing stress occurs between water layers near the interface and in a plane parallel to the surface. This is analogous to the tendency of a film of oil to remain at the water surface, although it occurs for a different reason. Thus, it is not at all difficult to conceive of a turbulent system in which the main body of fluid is quite well mixed and homogeneous, but in which surface volume elements are not replaced by others from below with as much freedom and as high a rate as might be expected. This imperfect mixing of the topmost and deeper water layers limits the rate of gas transfer, because gas transfer must originate at the surface,

and so the effective mixing rate for gas transfer is slower than the apparent rate calculated on the basis of simple hydraulic considerations. However, it should be clear that this surface layering tendency is a hydrodynamic property of the fluid, and does not reflect the existence of a liquid film of finite thickness in which only molecular diffusion can take place.

Unfortunately, by its very nature, turbulence itself cannot be independently or directly observed or measured, even though it can be defined and treated mathematically. Instead, it can only be observed in terms of the actual dispersion of a tracer substance of some sort that can faithfully indicate the behavior and movement of the fluid volume elements. Such a tracer substance, to be a true indicator of turbulent mixing, must actually become an intimate part of the fluid volume elements and thereafter remain fully associated with them. For example, discrete particles that sink or float because of their density cannot be accepted as a suitable tracer for turbulent mixing, no matter how tiny they may be, because they may not indefinitely remain intimately associated with all of the fluid volume elements. Similarly, tracer solutions (such as a salt solution) that significantly differ in specific gravity from that of water may not faithfully indicate for long the movement of all of the volume elements of water.

As a result, although gas transfer is primarily a function of turbulent mixing, the rate of gas transfer cannot be accurately predicted in terms of turbulence because turbulence itself cannot be independently observed or known. Indeed, for obvious reasons a dissolved gas has much to recommend it as the ideal tracer for turbulence, and it is much more likely that the reverse will prove more practical, namely, that the real measurement of turbulence will be accomplished in terms of accurate observations of gas transfer.

The mathematical developments that are commonly used to describe turbulence are beyond the scope of this report and aside from its purposes. However, a few examples, given below, will be useful as a means of illustrating the problems associated with attempts to define and observe gas transfer and reaeration in terms of turbulence.

Experimental Systems.—A number of different laboratory scale experimental systems have been designed and used for observing gas exchange in mixed water systems. Several kinds of turbulent mixing devices have been used, including stirring mechanisms, oscillating grid devices, and recirculation of the water. In other experiments, the gas has been bubbled through the water.

The constant pressure gas transfer reactor utilized by Hutchinson and Sherwood [3] is typical of systems employing a stirring device, and provided considerable useful information regarding the absorption of gases by water. In this experimental system the absorption of a test gas by initially degassified water was measured in a closed constant pressure reactor. For each such test, mixing at a fixed rate was accomplished by means of a stirrer connected by a central shaft passing through the bottom of the reactor to an external motor. The test gas pressure in the space above the water was kept constant by an arrangement that permitted the total gas volume to decrease as test gas was absorbed by the water. The test gas absorption curve was thus obtained in terms of the cumulative reduction of gas volume, and the gas transfer coefficient was then derived by usual methods.

A number of test gases were studied over a range of stirrer speeds. The degree of turbulent mixing was obtained in terms of the speed of rotation of the stirrer in revolutions per minute, and no other measure of mixing was indicated. Analysis of the resulting data indicated that reproduction of the mixing characteristics from one test to another on the basis of stirrer speed was generally good at intermediate to higher speeds, but not so dependable at the lower rates of stirring. Analysis of the reported gas exchange coefficients at the intermediate stirrer speeds provides some insight into the relative exchange capabilities of various gases, and will be considered in greater detail later in this report. The reader is referred to the original paper for further details of this experiment.

A closed constant pressure gas transfer reactor was also used by Dobbins [4] in later studies of the exchange capabilities of several gases. In these experiments, turbulence was produced by the use of a stainless steel lattice, or grid, oscillated in the vertical direction in simple harmonic motion. The lattice was connected by a vertical central shaft to a motor mounted above the reaction vessel, the shaft passing through the top of the reactor via a rubber bellows. Gas absorption by the initially deaerated test water was measured in terms of the accumulated volume of small increments of water that had to be added to maintain constant gas pressure. The degree of turbulent mixing was represented by the number of oscillations per minute and the length of stroke of the moving lattice. Details of this experimental system

are provided in the original paper, and the resulting gas exchange coefficients for the several gases that were studied will be discussed later in this report. O'Connor and Dobbins [5] employed a similar harmonically oscillating lattice system in earlier experiments on oxygen transfer, but in that case dissolved oxygen concentrations were measured directly.

A recirculating open reactor system was used by Tsivoglou et al.[6] as a means of studying the relative transfer capabilities of pairs of gases. In these experiments, the test water was recirculated at a constant rate by means of an external pump, and passed from the bottom of the reactor vessel through the pump, then through several external gas concentration measuring devices, and then back into the reactor at the bottom. This system was designed specifically to permit simultaneous measurement of the transfer of two gases, oxygen and a tracer gas; this assured truly identical mixing for the transfer of both gases in any single experiment, and so completely avoided the problem of attempting to measure or define the existing turbulence. Figure 1 (see ch. II) is a schematic drawing of the experimental system, and the experimental details are described later in this report. The degree of turbulent mixing in these tests was not defined, as it was not required information. However, attempts to relate the observed gas transfer coefficients to the recirculation rate, measured as $\frac{Q}{V}$ (flow divided by volume), indicated that some short-circuiting did take place. This in no way affected the ratio of gas transfer coefficients, although it did affect the individual values. These experiments provided the basis for the subsequent laboratory and field studies, reported in later chapters, on tracer measurement of stream reaeration capacity.

These brief descriptions of typical experimental systems for studying gas transfer clearly demonstrate the difficulty associated with any attempt to relate gas exchange coefficients to turbulence. In no case was the investigator able to evaluate mixing or turbulence in a fundamental way. Each method of providing mixing of the water was quite different from the others, and in each case the method of evaluating mixing was system-dependent and mixing was imperfect. In the Hutchinson and Sherwood system the stirrer produced rotational flow, and a vortex was observed at the higher stirrer speeds. The oscillating grid used by Dobbins and by O'Connor and Dobbins produced vertical agitation of the volume elements of water, and volume elements near the bottom of the cylinder may well have stayed at the bottom indefinitely, even though they were in a state of constant motion in that immediate locale. Short-circuiting to an undetermined degree occurred in the recirculating water system of Tsivoglou et al. Thus in each system it appears most unlikely that the mixing was truly homogeneous in the sense previously described. It is quite impossible to accurately relate the r.p.m. of Hutchinson and Sherwood to the oscillations per minute of Dobbins or to the apparent recirculation rate of Tsivoglou et al., except in terms of the gas exchange coefficient itself. There is therefore no independent way by which the gas transfer coefficients observed in one system can be related to those observed in another in terms of presently available measures of mixing or turbulence.

It is especially important to note also that within any of these individual experimental systems it is impossible to be certain that the same actual conditions of mixing are reproduced from one experiment to another. Such systems are quite sensitive to what may appear to be minor changes in the depth, centering or speed of the stirrer or lattice, or of the recirculation rate, and such changes may significantly modify the actual mixing characteristics, particularly at the water surface, from one test to the next. The r.p.m. of the stirrer, the oscillations per minute and the apparent recirculation rate are not, by themselves, accurate measures of mixing. For similar reasons, the amount or rate of energy expended on mixing can be no more than a relative, system-dependent, measure of mixing. As there is no basic means of observing the actual degree of mixing in any test, there can be no way of knowing that fully identical mixing conditions have occurred in two or more tests.

Natural Streams.—In natural streams the situation is considerably worse, so far as independently measuring or knowing mixing or turbulence is concerned. In contrast to the geometrically simple vessels and mixing devices that can be employed in the laboratory, a natural stream channel is anything but uniform in terms of the physical characteristics that influence mixing. For example, in any stream reach of practical length, significant and abrupt changes in width, depth, slope, channel direction, velocity and/or bottom roughness may occur, and will affect the degree of turbulent mixing and the resultant gas transfer characteristic; the presence of spillways or falls, riffles and pools are indicative of such changes. Heavy

growths of water plants or the entry of substantial tributary or waste flows can also modify downstream mixing characteristics. Other factors, such as wind direction and speed, may also significantly modify mixing, and the presence of pollutants such as detergents can alter the gas exchange capability of the water itself. Certain of these factors undoubtedly affect mixing, surface replacement and gas transfer capacity more strongly than others; some of them, such as slope and velocity, are not mutually independent. In some cases, a general relation between mixing and the individual factor can be formulated on a rational basis, but even then the application to real stream reaches requires the introduction of an empirically determined coefficient that cannot be directly applied to other stream reaches. The effect on mixing and surface replacement of factors such as bottom roughness is virtually impossible to define and evaluate with dependable accuracy, as roughness itself is not susceptible to direct or independent measurement.

As a result, it has not proved possible to independently measure or evaluate mixing or turbulence in natural streams. For reaches of practical length, say one-quarter mile or more, the assumption of uniform mixing and a predictable, uniform rate of replacement of the surface water layers cannot safely be made. Shallow, faster streams are likely to consist of alternating riffled and pooled reaches of variable length, whereas deeper, slower rivers with a more uniform channel are more susceptible to the development of a semi-laminar surface that is only inefficiently replaced by water from the deeper regions of flow. In brief, it must be presumed that no two river reaches are identical, so far as mixing, turbulence and gas exchange capacity are concerned. In fact, these properties most probably change significantly from point to point within most reaches, and are anything but constant over long distances.

Available procedures for estimating the reaeration capacity of natural streams generally require the assumption of uniform mixing and turbulence over relatively long stream reaches. In particular, they treat reaeration as a single first-order process over substantial distances, as no other practical alternative has been available. This has been the only fruitful and practical approach possible, and, cautiously applied, does not necessarily lead to large error in estimates of the reaeration capacity. However, it is decidedly an averaging procedure rather than an exact one, as the reaeration rate coefficient itself undoubtedly varies substantially within most such river reaches.

The tracer method described in the following sections of this report requires no such assumptions as to uniformity of mixing or turbulence, or constancy of the reaeration rate coefficient. It provides a direct and quite independent measure of gas exchange capacity under existing conditions of mixing and surface water replacement, whatever they may be.

HISTORICAL BACKGROUND

The purpose of this section of the report is to present a brief outline of the development of information regarding the reaeration capacity of streams and to summarize the current state of the art of predicting stream reaeration capacity. The historical development of knowledge and information directly related to reaeration goes back to the early part of the century, and this history is a worthy subject for an entirely separate report. In addition, substantial bodies of information exist in the general areas of diffusion of gases in water and the hydrodynamics of fluids in motion, and much of that information is relevant to the subject at hand. It is not the purpose here to present an exhaustive and comprehensive review of all of the available relevant literature. Instead, this section is limited to a brief presentation and discussion of current concepts and models commonly used for predicting stream reaeration capacity, and a brief summary of the associated assumptions and problems.

Models for Reaeration Capacity

The general mathematical form for describing the process by which oxygen (and other gases) will become dissolved in water is the well-known expression

$$\frac{dD(t)}{dt} = -K_2 D(t) \qquad (1)$$

in which D(t) is the dissolved oxygen concentration deficit below the saturation limit, in mg/l, at time t, and K_2 is the reaeration rate coefficient, with units of reciprocal time. In this form, $D(t) = C_s - C(t)$, where C_s is the dissolved oxygen saturation limit, and C(t) is the dissolved oxygen concentration at time t, both in mg/l.

Equation (1) states simply that the rate of change of the saturation deficit with time is proportional to the deficit at any time. This hypothesis

was applied to the reaeration problem more than 40 years ago [7 8] and is fully explained and developed in the classical work of Streeter and Phelps on the oxygen sag self-purification model.[7]

Equation (1) is solved by

$$D(t) = D_a e^{-K_2 t} \quad (2)$$

where D_a is the initial dissolved oxygen saturation deficit. It has become customary to apply equation (2) in a slightly different form

$$D(t) = D_a \times 10^{-k_2 t} \quad (3)$$

for purposes of reducing it to common logarithms. This conversion is accomplished by noting that

$$K_2 = 2.303 k_2 \quad (4)$$

Both the solubility of oxygen (C_s) and the reaeration rate coefficient are functions of temperature, hence equations (1) and (2) are valid at constant temperature. The current literature still contains some disagreement regarding the exact oxygen saturation limits for stated temperatures, as well as regarding the exact manner in which K_2 is related to temperature, but the extent of these disagreements is negligibly small compared to the range of error usually associated with numerical estimates of K_2 in natural streams.

(Because of the importance of full understanding of the basic reaeration process, equations (1) and (2) are derived at a later point in this report from simple and basic considerations of the kinetics of gases. These derivations also lead to a firm quantitative evaluation of the dependence of K_2 on temperature, and demonstrate the relationship between temperature and dissolved oxygen saturation limits.)

Equations (1) and (2), in one form or another, are generally regarded as the basic law for the absorption of gases by water, and this law is widely accepted and applied in gas absorption experiments of all types. The reaeration rate coefficient, K_2, is, however, a general measure of gas exchange capacity; it includes the effects of both molecular diffusion of the gas and dispersion, or mixing, but is not sufficiently specific to permit knowing or evaluating these effects separately. Although K_2 can be evaluated within narrow limits in controlled laboratory experiments, in natural streams it cannot be directly observed because of the simultaneous occurrence of other processes that influence dissolved oxygen concentration. Because mixing cannot be independently known, the numerical value of K_2 cannot be predicted on the basis of the separate effects of diffusion and dispersion. This has led to the traditional indirect method of Streeter and Phelps by which a mean K_2 is calculated on the basis of the oxygen sag equation (or some modification) and attempts to measure the oxygen effects of the other processes. As has been noted, this indirect method has proved inadequate, and values of K_2 determined by it are always subject to doubt and often include substantial error.

As a result of these difficulties, a number of investigators have developed models for the independent prediction of values of K_2 on the basis of available knowledge on turbulence and the diffusivity of oxygen in water. The primary objective of such investigations has been to more specifically define the reaeration rate coefficient in terms of readily observable hydraulic factors such as depth and velocity of stream flow, channel slope, etc., on the assumption that the degree of mixing and surface renewal (and therefore K_2) can be related to these factors with sufficient accuracy. This would permit the prediction of specific values of the reaeration rate coefficient for specific stream reaches. The several models and approaches in current use are outlined briefly below. The reader is urged to consult the individual original publications for the detailed mathematical developments and especially for the associated assumptions.

(For convenience in the following discussion, K_2 will be treated as a single constant for any river reach; however, it should be borne in mind that the single value referred to is really an average of many individual values within the reach.)

Black and Phelps.[9]—In a 1911 report on the pollution of New York Harbor these authors presented the earliest model that has been applied to the problem of expressing the reaeration rate coefficient in terms of hydraulic parameters. This model was developed on the basis of application of Fick's law of diffusion, which states that the rate at which oxygen is transferred by molecular diffusion through the depth of a quiescent body of water is proportional to the surface area and to the oxygen concentration gradient in the direction of transfer. The model that was developed took the form

$$D(t) = Da \times 0.811 \left(e^{-K} + \frac{e^{-9K}}{9} + \frac{e^{-25K}}{25} + \ldots\right) \quad (5)$$

where

$$K = \frac{\pi^2 at}{4L^2} \quad (6)$$

The terms in equation (5) are the dissolved oxygen saturation deficits, as defined earlier, and in (6), the constant, a, is taken to be the coefficient of molecular diffusion of oxygen in water, L is the depth, and t has been defined as a "mixing period," or a time of exposure of water at the surface. Phelps [10] envisioned reaeration as taking place due to two processes, namely surface solution and subsurface diffusion. In this view, oxygen enters the water by solution at the immediate surface of contact, which he regarded as an infinitely thin film in which saturation is achieved practically instantaneously. Subsequently, oxygen is transferred to the lower layers by diffusion. Mixing of the water layers causes ". . . an intimate admixture of very thin layers of saturated water and relatively much thicker layers of unsaturated water . . . ." and oxygen is transferred to the unsaturated layers by diffusion. This concept of turbulent mixing envisioned, for convenience, periods of complete quiescence alternating with complete and instantaneous mixes. The length of the quiescent period in any case could then be regarded also as the period of exposure, t in equation (6).

Velz [11] later applied data obtained by Streeter, Wright and Kehr [12] to show that, in the experimental channel studies conducted by those investigators, the mixing period of Black and Phelps could be related to the depth of flow in the experimental channel. Velz also developed a nomograph to facilitate solution of the Black and Phelps equation, and this is used together with a chart defining the mixing period in terms of depth of flow. It has been noted elsewhere [5] that in equation (6) the value that was determined earlier for the coefficient, a, must have included the effects of both molecular diffusion and dispersion.

Streeter and Phelps.[7]—These authors utilized data gathered in extensive studies of the pollution and purification of the Ohio River to develop in 1925 the earliest model for self-purification of a polluted stream, the famous oxygen sag equation, which is still regarded as the basic expression for stream self-purification and is still widely applied to specific pollution problems. Using this equation, and applying the indirect method referred to earlier, the numerical values of K_2 were calculated for various reaches of the Ohio River and for a range of flow within these reaches. Postulating that these values should be related to temperature, stream depth, and turbulence, Streeter and Phelps then proceeded to develop an empirical model defining the reaeration rate coefficient in terms of the hydraulic factors, temperature being considered constant.

Noting the earlier work of Black and Phelps, and reasoning also from hydraulic considerations, Streeter and Phelps indicated that the reaeration rate coefficient should be roughly proportional to the reciprocal of the square of the water depth. They reasoned further that turbulence might be expected to follow the form of a power function of the velocity of flow. Combining these concepts, they arrived at the empirical model

$$K_2 = \frac{cV^n}{H^2} \qquad (7)$$

where H is the depth and V the velocity of flow, and c and n are constants that must be determined empirically. Their comments in regard to the character of turbulence are still worthy of note, and were as follows:

". . . the turbulence of a stream is an abstract function dependent upon and capable of expression only in terms of some other more concrete stream characteristic. For a given stream type, some definite relationship might reasonably be expected to exist between the turbulence of a stream and its velocity of flow, but it is evident that different types of streams should reveal quite different velocity-turbulence relations. . . . No very definite theoretical relation exists between turbulence and velocity, even assuming other physical conditions constant. In a general way, turbulence is the result of frictional resistance to flow, and under uniform physical conditions might be expected to be a power function of the velocity of the form:

$$T = cV^n$$

the constants c and n defining the stream type as regards the fixed physical conditions, such as slope, character of bottom, depth, shape, and direction of channel, etc. This subject can therefore be dealt with only empirically."

In their studies of the Ohio River, Streeter and Phelps applied the values of K_2 calculated by their indirect method, together with observed velocities and depths, to obtain empirical values for the coefficients c and n in equation (7). The numerical values used for H in equation (7) were the depths above extreme low water. For each reach of the Ohio River that was studied, a number of observations were made, and mean values of c and n were derived. It was found that the values of n so obtained varied from 0.57 to 5.40, and that the associated values of c ranged from a low of 0.23 to a high value of 131. These investigators cautioned as follows, in regard to the general application of their work:

"The empirical relationship established with respect to reaeration rates in the Ohio River must be interpreted, for the present at least, as applicable only to this stream or to rivers of a closely similar type as regards their physiography. Further studies of these relations will doubtless reveal wide variations in the specific values

of constants derived for streams of different types, and will probably also disclose the formulas expressing them do not always follow the same mathematical laws as found in the present case."

O'Connor and Dobbins.[5]—In 1956, these investigators presented an analysis of the relationship between stream reaeration and turbulence, based upon theoretical consideration of both processes. They accepted the basic reaeration model, equation (1), and, working with the Lewis and Whitman two-film theory and Fick's law of diffusion, they developed an associated theory of turbulence by introducing such concepts as the Prandtl mixing length and Danckwerts' hypothetical age distribution of surface volume elements, and relating these to a rate of surface renewal. They reasoned that surface volume elements of water contain a dissolved oxygen concentration equal to that of the main body of fluid at the instant they reach the surface, that they then become saturated instantaneously, and that the oxygen transfer across the surface is accomplished by molecular diffusion. These authors also discuss the existence of a laminar film at the water surface, and the alternative of periods of complete quiescence followed by instantaneous vertical mixing as proposed by Phelps, in terms of the mathematical implications and convenience.

Laboratory experiments were conducted using the oscillating grid system described earlier, and a close empirical relationship between the frequency of oscillation of the grid and the observed reaeration rate coefficient, K_2, was demonstrated. O'Connor and Dobbins reasoned that this relationship supported their proposed relationship between K_2 and the rate of surface renewal, which is not observable.

Considerations and hypotheses such as those noted led O'Connor and Dobbins to the following models for the reaeration rate coefficient:

(A) *Isotropic Turbulence*

$$k_2 = \frac{(D_L U)^{1/2}}{2.31\, H^{3/2}} \qquad (8)$$

where D_L is the diffusivity of oxygen in the liquid film, U is the mean forward flow velocity, and H is the mean depth. The similarity of form of this relationship to the Streeter-Phelps relationship for the Ohio River, equation (7), is worthy of note.

(B) *Nonisotropic Turbulence*

$$k_2 = \frac{480\, D_L^{1/2} s^{1/4}}{H^{3/4}} \qquad (9)$$

where s is the slope of the river channel, and the other terms are as defined above. In the original paper, the authors indicated that for any specific river reach the selection of the best equation to use for the reaeration coefficient could be based upon an estimate of the Chezy coefficient. Experience since that time has apparently led to the common application of equation (8), the isotropic turbulence case, in most if not all situations.

For verification of their theory, as represented by the foregoing equations, O'Connor and Dobbins presented a graphical comparison of k_2 values calculated according to their theory with k_2 values previously reported by others for various river reaches. The values reported by others, referred to as "observed" values, were obtained by the indirect method of oxygen sag analysis referred to earlier in this report, and, in making the comparison, O'Connor and Dobbins attempted to select only river reaches in which they believed sludge deposits and algal effects to be minimal. Their graph indicates that, for the comparisons shown, the calculated and "observed" values of k_2 might differ by a factor of as much as 1.5.

For further details regarding the theoretical developments related to equations (8) and (9) and the various assumptions involved, the reader is urged to consult the original reference.

Churchill, Elmore, and Buckingham.[13]—These investigators attacked the problem of evaluating reaeration in terms of hydraulic stream characteristics on an empirical rather than a primarily theoretical basis. Their extensive field studies were conducted in stream reaches below deep storage impoundments, where water released from subsurface locations contained relatively little dissolved oxygen during the summer and fall seasons due to the prolonged storage and thermal stratification that had occurred. In order to avoid, insofar as possible, the problems associated with the Streeter-Phelps indirect method of calculating K_2, and to limit the number of hydraulic variables, their studies were carefully restricted to stream reaches that: were below reservoirs that released water relatively low in dissolved oxygen and B.O.D.; were near enough to the point of release to still have relatively low dissolved oxygen at the upstream end of the reach to be studied; were relatively uniform in slope, depth and shape of cross-section; were long enough for an observable change in dissolved oxygen to occur; contained no large tributaries; were practically free of dissolved B.O.D. and organic bottom deposits. The studies were all conducted under conditions of steady stream flow, by arrangement for steady releases at the upstream hydro plant.

As a result of the above restrictions in regard to the reaches that were accepted for study, the observed dissolved oxygen changes within the reaches were small, usually in the range of 0.2 to 0.4 mg/l; times of flow were usually in the range of 10 to 20 minutes. In order to obtain sufficient data for accurate estimates of k_2, therefore, the typical study consisted of measuring the dissolved oxygen concentration at the upstream and downstream ends of a reach over a period of 15 to 18 hours, repeating the measurements each hour. Cross-sectional sampling was performed, and the absence of a vertical dissolved oxygen gradient was verified. Sample collections at the downstream end of the reach were delayed over those at the upstream end by a period equal to the mean time of flow. The photosynthetic and respiratory effects of algae and other aquatic plants were observed in some reaches, and the hourly field sampling, together with other work, was used as a basis for correction of the field data for these effects.

For each reach the 15 to 18 individual values of k_2 were calculated according to the basic reaeration model, using a two-point form of equation.[2] Both the dissolved oxygen saturation values used and the effects of temperature on k_2 were verified by separate experimental studies. A total of 509 separate observed values of k_2 was thus obtained. By the use of dimensional analysis and multiple regression techniques, the observed mean values of k_2 were related to the hydraulic characteristics of the river reaches studied. Several equations relating the reaeration capacity to the various hydraulic variables were thus developed and tested. Of these, the authors have indicated the following equation to be most suitable and useful for predicting values of k_2:

$$k_2 = \frac{5.026\ V^{0.969}}{H^{1.673}} \qquad (10)$$

at 20° C., and where V is the mean velocity of flow, and H is the average depth. In this regard, the authors indicate that the mean velocity is best obtained from a calculation of flow divided by the average cross-sectional area, and that the mean depth should be obtained by dividing the average cross-sectional area by the average width of a reach. The authors caution in regard to the application of equation (10) that it should not be applied in reaches where a significant amount of "white water" occurs, nor where vertical stratification exists, and point out that the predicted values of k_2 should be corrected for the effects of pollutants on reaeration and oxygen solubility, as the equation was developed from studies of unpolluted water. They indicate also that for many applications, equation (10) can be simplified to:

$$k_2 = \frac{5\ V}{H^{1.67}} \qquad (10')$$

The similarity of mathematical form of equation (10) to the equation proposed by Streeter and Phelps, equation (7), and to the O'Connor-Dobbins equation for isotropic turbulence, equation (8) should be noted. In the case of equation (10), Churchill et al. have also provided a graphical comparison of the predicted and observed k_2 values for the reaches studied. For each reach, the predicted value of k_2 was plotted against the geometric mean of the 15 to 18 individual k_2 values that were observed during the sampling period. It may be seen from the graph that individual observed average values of k_2 differ from the associated calculated values by a factor of as much as 2.0 or slightly more, for these selected reaches. The reader is encouraged to refer to the original publication for further details regarding these extensive studies of the relation between the reaeration capacity and the hydraulic characteristics of a natural stream.

Other Reaeration Models.—It has been the intention here to briefly present the reaeration models that are currently in common use, and thus to summarize current approaches to evaluating or estimating the reaeration capacity of a natural stream. Other approaches and other reaeration models have been developed and are available, but are not widely used as yet. It is suggested that the interested reader refer particularly to the work of Krenkel and Orlob,[11] who have investigated the potential relation between reaeration and longitudinal dispersion, and to the recent studies of Dobbins.[15]

Summary

As has been indicated, the basic reaeration model, equation (1), is quite generally accepted and widely applied, and has served as a basic starting point for development of the more recent mathematical models that attempt to relate reaeration capacity to the hydraulic characteristics of a river reach. The principal problem that is readily traced through the developments of the several reaeration-turbulence models that are now available relates directly to our inability thus far

to measure either reaeration capacity or turbulence in any accurate, truly independent fashion in the field situation. The available theoretical developments require assumptions that cannot be rigorously proved, regarding the relationship of reaeration capacity to such conceptual but non-observable parameters as the mixing length, the frequency of mix, the rate of surface renewal, etc. Thus, except for equation (1) itself, all of the available models must, at this stage, be regarded as possible but not proved, and therefore as empirical expressions that cannot safely be extrapolated to become generally applicable. In another sense, what has been lacking has been a full evaluation of the range and kind of error associated with the predictions of the various models.

As has also been noted, the most commonly used models for predicting reaeration capacity as a result of turbulence take the form

$$k_2 = \frac{c\,V^n}{H^m} \qquad (11)$$

as proposed by Streeter and Phelps in 1925, where V is the mean velocity of flow and H the average depth, and c, n, and m are coefficients that must be determined empirically for specific reaches. In applying this form, Streeter and Phelps reasoned that the coefficient m could be fixed ($m = 2$), and their derived average values of c and n varied greatly for the several reaches of the Ohio River that were studied. They cautioned against extrapolation to other reaches or other rivers. Churchill et al. chose instead to evaluate all three coefficients empirically by multiple regression techniques, based on field studies of reaeration in selected reaches of Tennessee Valley Authority streams. The comparisons presented by Churchill et al. indicate that, even for river reaches that are carefully selected for physical uniformity, the predicted average value of k_2 may differ from the observed mean value by a factor of at least 2.0 in a specific reach. It appears clear that considerably larger differences between individual observed and predicted values of k_2 must be expected if that model is applied more generally to longer river reaches that are less uniform in slope, depth, cross-section, roughness, etc. The selective comparison of "observed" and predicted values of k_2 presented by O'Connor and Dobbins is less readily interpreted, as the "observed" values were in fact not observed at all, but were values calculated by a number of other investigators by use of the indirect Streeter-Phelps oxygen balance method and with the usual assumptions as to the absence of algal effects, bottom sludge oxygen demands, etc. There is no apparent reason why the agreement between observed and predicted values of k_2 should be any closer by the O'Connor-Dobbins model than was found by Churchill et al., or by Streeter and Phelps.

No two reaches of natural stream can safely be presumed to be truly identical so far as mixing, turbulence, and gas exchange capacity are concerned, it must be recognized that the development of models such as those that have been described requires a good deal of averaging, in the sense of obtaining mean depths, mean velocities and mean values of k_2 from average cross-sectional areas, average widths and average observed dissolved oxygen concentrations. The evaluation of average depth itself, and the real meaning of the derived numerical value, is not simple when it is recognized that 100 feet of riffle or a small waterfall in a half-mile reach of stream probably adds significantly to the actual reaeration capacity of the reach. Nor is reaeration of a natural stream actually a simple first-order reaction, with a single constant value of K_2, in river reaches of practical length. As a result, it has not been possible to know which of the available reaeration-turbulence models is likely to yield the best results, or, more importantly, the full extent of the associated error of prediction in any case.

A sound mathematical expression relating reaeration capacity to the simple hydraulic characteristics of a stream would clearly be of great advantage in planning for pollution control and water resources development, and it is not the intent of this brief review to minimize the importance and the real value of the models that have already been developed. However, it is clear that the several available models must all be regarded as empirical rather than truly general, and that the error of prediction associated with any of them may be quite large. As has been noted, such errors are directly reflected in the estimated necessary costs of waste treatment for pollution control, and it is therefore imperative that more dependable and accurate methods of measuring or predicting stream reaeration capacity become available.

GENERAL OUTLINE OF THE TRACER METHOD

As indicated in the earlier paper on this subject,[6] the studies reported in the following chapters of

this report were designed to develop field methods for accurately determining the reaeration capacity of a stream, on the basis of a series of analogies and by the simultaneous use of several tracers. The first phase of the work, reported in part in the earlier paper, consisted of selecting a suitable gaseous tracer for oxygen and of establishing its gas exchange capacity relative to that of oxygen. Following the successful completion of this task, the second phase of the studies would consist of demonstrating the field application of the tracer method by using the gaseous tracer directly in a natural stream together with a second nongaseous tracer that would indicate dispersion alone. The second tracer would permit correction of the observed tracer gas concentrations for dispersion, thus permitting accurate evaluation of the loss of tracer gas to the atmosphere in any river reach. The oxygen exchange capacity could then be obtained on the basis of its known gas exchange capacity relative to that of the tracer gas.

The basic assumptions associated with this approach, and upon which its success depends, are as follows:

(1) The nongaseous dispersion tracer undergoes only dispersion in the stream, and is not adsorbed on the stream bed or otherwise lost in any significant amount.

(2) The dissolved tracer gas undergoes dispersion to the same degree as the nongaseous dispersion tracer, and in addition is lost to the atmosphere; it is not otherwise lost by adsorption or other processes in any significant amount.

(3) The tracer gas and oxygen undergo gas transfer to the same relative extent, and the ratio of their respective K_2 values is not significantly affected by temperature, turbulence, or the presence of usual water pollutants, in the range of interest.

It is emphasized that the tracer method constitutes a direct measure of gas exchange capacity under existing hydrodynamic conditions. As a result, a number of other assumptions are not necessary and are not associated with the tracer method. Specifically, no assumption is made regarding the uniformity of the channel (cross-section, depth, slope, roughness, etc.), and no assumption is made as to the uniformity or nonuniformity of mixing. No assumptions as to frequency of mix, mixing length or rate of surface renewal are required, and it is not necessary to assume that reaeration took place in the field as a simple first-order process with a single constant value of K_2.

The tracer gas finally selected for use was krypton-85. Krypton is a monatomic, or "noble" gas that is chemically inert. The radioactive isotope, krypton-85, is susceptible to highly sensitive methods of measurement. It has a half-life of 10.3 years, and so radioactive decay during laboratory tests or field application is quite negligible. This tracer gas therefore meets the requirements of assumption (2) above, so far as losses are concerned.

The dispersion tracer selected for field use was tritium, in the form of tritiated water. It is no more subject to adsorptive or other losses than ordinary water itself, because it is water, and so constitutes the ideal dispersion indicator, so far as assumption (1) above is concerned. (Losses of water due to evaporation or seepage into the stream bed can usually be taken to be negligibly small in river reaches of length of interest. In any event, however, the tritiated water and the dissolved tracer gas will normally be lost to the same degree, and so the observed gas exchange capacity will not be affected.) Tritium is also radioactive, and therefore susceptible to very sensitive methods of detection and measurement. Radioactive decay during the times of interest is also completely negligible.

Assumption (3) above has been the subject of considerable laboratory investigation, as reported in part in the earlier paper and as reported in full detail in Chapter II of this report. These studies have demonstrated clearly that in fresh water the relative exchange capacities of krypton-85 and of oxygen are a function of the molecular properties of the gases, and that the ratio of K_2 values is not significantly affected by temperature, turbulence or the presence of pollutants within the range of interest. As shown in chapter II, the ratio of K_2 values for krypton-85 and oxygen can be regarded as a firmly established constant, fully applicable to the field situation.

Two additional conditions are necessary for the successful application of the field tracer method for reaeration. First, the tracer gas must be fully and truly dissolved in the water that is used for dosing the stream if it is to faithfully indicate gas exchange capacity. Secondly, if the tritiated water is to indicate accurately the degree of dispersion of the tracer gas, not only must the two tracers be released as a truly simultaneous dose, but also their concentrations must both be measured in the same downstream sample. These conditions have

been met by the field and laboratory methods described later, and so the other part of assumption (2) above is valid.

Finally, in the field application a third tracer, rhodamine-WT dye, is released simultaneously with the other two. Monitoring with continuous-flow recording fluorometers is conducted at the selected downstream sampling points, and the dye tracer thereby serves the purposes of indicating time of flow and longitudinal dispersion in the reach, as well as indicating when to sample for the other tracers. Unfortunately, the dye does suffer adsorptive losses, otherwise it could replace the tritium as an accurate indicator of total dispersion.

Full details of the laboratory investigations and the field demonstration of the tracer method, together with methodology and typical computations, are contained in the following chapters of this report.

Validity of the Tracer Method

With the development of any new method of measurement, it is customary to present a clear statement of the assumptions that have been made, an estimate of the likely range of associated error, and a proof. The assumptions that have been made in connection with application of the tracer method have been stated above. An estimate of the range of error associated with tracer measurements of stream reaeration capacity is presented later as a part of a discussion of the observed degree of reproducibility of successive field measurements.

The tracer method for measuring stream reaeration capacity is quite straightforward and involves no special problems or assumptions other than those that have already been stated. The key assumption is the third, namely that the ratio of the exchange capacities of krypton-85 and oxygen is constant, and the validity of this assumption has been thoroughly demonstrated by the work reported in Chapter II. Thus, the method is proved in terms of the clear validity of the above assumptions.

Although it would be easy to perform, comparison of the tracer-determined oxygen transfer capacities with values obtained by the indirect oxygen balance method would in no way constitute a "proof" or a valid test of the tracer method. On the contrary, values of K_2 calculated by the indirect method are no more than estimates at best, and one would be attempting to test an accurate direct measurement by comparing it to a much more dubious estimate. There is no other way of measuring or knowing stream reaeration capacity, and thus tracer measurements of oxygen exchange in streams constitute the primary and independent measurements against which other estimates of reaeration, whether by oxygen balance or by empirical predictive models, can properly be tested. Comparison of the tracer-determined reaeration capacities of several reaches of the Jackson River in Virginia with values predicted by the O'Connor-Dobbins and the Churchill predictive models are therefore presented later in the report as a means of evaluating the range of error associated with the predictive models.

relative transfer properties of gases

CHAPTER TWO

INTRODUCTION

In order to utilize krypton-85 as a tracer gas for the evaluation of the transfer of oxygen by reaeration in turbulent natural streams, it is necessary to firmly establish the relative transfer capabilities of the two gases in turbulent water systems. The rate of gas transfer is directly dependent on the degree and kind of turbulence, but turbulence cannot be directly or independently evaluated. Hence, initial experiments to evaluate the relative transfer abilities of krypton-85 and oxygen in a turbulent water system were designed to permit observation of the simultaneous transfer of both gases in a single recirculating turbulent water reactor. It was thus assured that the degree of turbulent mixing was truly identical for the transfer of both gases in each individual test, and the problem of evaluating turbulence was in that way avoided. These initial tests evaluated the relative gas exchange capabilities of krypton-85, oxygen, and radon-222, and established the necessary basis for the use of krypton-85 as a tracer for oxygen in turbulent streams. These tests have been reported in detail in an earlier paper,[6] and will be summarized briefly in the following text.

The early tests with krypton-85, radon-222, and oxygen, although complete and adequate in themselves as a basis for the field use of the tracer method of evaluating stream reaeration, raised other interesting and relevant general questions regarding the transfer properties of gases in turbulent water systems. Therefore a second series of tests was conducted with other gases, including hydrogen, helium, nitrogen, oxygen and stable krypton, each in combination with trace quantities of krypton-85. These tests, and their results, are reported in detail here also.

EARLIER TESTS—OPEN REACTOR

Reactor I consisted of an open cylindrical recirculating water reactor, with external appurtenant equipment as shown in Figure 1. The reactor and most of the external tubing were immersed in a constant temperature bath. Two reactors were used, one of 10-inch and one of 12-inch diameter, each 12 inches deep.

Referring to Figure 1, the test water flowed out of the bottom central reactor outlet, through the pump, and then portions were diverted through a dissolved oxygen (D.O.) galvanic probe chamber, a water-jacketed flow-through Geiger tube, and a

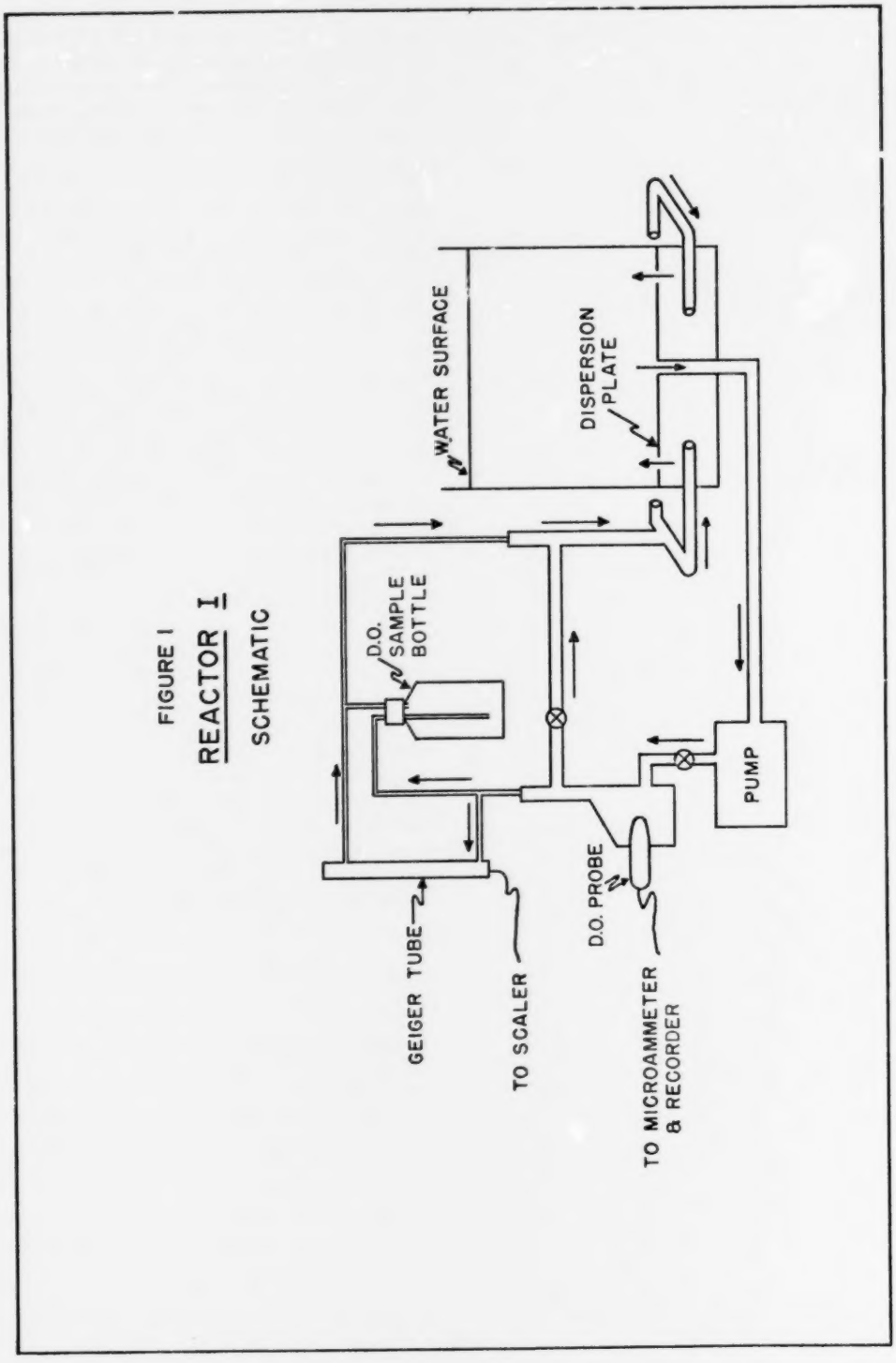


FIGURE I

REACTOR I

SCHEMATIC

sample bottle (for measurement of D.O. by the Winkler [16] method). The recombined flow returned to the reactor under a dispersion plate located at the bottom of the reactor vessel, and entered the reactor through a set of peripheral holes in the dispersion plate. Details of construction and operation of the system are contained in the earlier paper.[6]

The general test procedure consisted of preparing initial test conditions such that the dissolved oxygen content of the test water was quite low, whereas the concentration of dissolved tracer gas was high. The test then proceeded at a fixed temperature and turbulence condition, and the simultaneous increase of dissolved oxygen concentration and decrease of tracer gas concentration were observed and recorded until the oxygen concentration approached its limiting (saturation) value. Since the water surface was open to the atmosphere, oxygen concentration in the test water approached, for any test, the limit associated with atmospheric oxygen concentrations; the tracer gas water concentration decreased toward zero, as no experimentally significant quantity of tracer gas was present in the atmosphere.

Figure 2 shows a typical set of observed concentration curves for an experiment in the radon-222 test series. The reactions involved were simple first order, as expected. D.O. concentrations followed the well known

$$D(t) = D_0 e^{-K_{ox}t} \qquad (1)$$

where D(t) is the oxygen deficit in mg/l below the saturation limit, at time, t, D_0 is the initial saturation deficit, and K_{ox} is the desired reaction rate constant. Radon-222 concentrations were described by

$$A(t) = A_0 e^{-(K_{Rn}+\lambda)t} \qquad (2)$$

where A(t) is the radioactivity of the radon in the water at time, t, (in pc/ml), A_0 is the initial activity, λ is the radon-222 decay constant (0.0075/hr.) and K_{Rn} is the desired reaction rate constant.

A series of such tests was conducted with krypton-85 and oxygen (26 tests) and with radon-222 and oxygen (20 tests) under various conditions of temperature (11° C. to 32° C.) and turbulence. The observed gas concentration curves for each such test were analyzed for the individual gas exchange reaction rate constants, and for each test the desired gas exchange coefficient ratio

$$\frac{K_{\text{tracer gas}}}{K_{\text{oxygen}}} \qquad (3)$$

was thus obtained. In addition, as a general test of validity of the experiments, in each case the observed oxygen saturation limit was compared to the known expected limit, and the agreement was generally very good. This general test of validity, together with the fact that the observed curves very closely followed the expected first order kinetics, fully verified the experimental approach, and indicated a quite small range of possible error.

These earlier open reactor experiments led to several important conclusions for the gases studied:

(1) The relative gas transfer capability of krypton-85 and oxygen, measured as the ratio of reaction rate constants [equation (3)], is 0.82, with a standard deviation of 0.04, the transfer of krypton-85 being the slower process. Thus, an observed reaction rate constant for krypton-85, determined from observed losses of the tracer gas, can be used to evaluate the reaction rate constant for reaeration, or the transfer of oxygen, under identical conditions in a turbulent system.

(2) Similarly, the relative gas transfer capability of radon-222 and oxygen is 0.70, with a standard deviation of 0.04, radon-222 transfer being the slower process.

(3) The above gas exchange ratios are not significantly affected by temperature in the range of 10° C. to 30° C.

(4) The gas exchange ratios are not affected or modified by the degree of turbulent mixing of the water in the range studied.

(5) The observed gas exchange ratios demonstrate clearly that Graham's Law, which expresses the relative diffusion rates of two gases in terms of their molecular weights, is not applicable to diffusion in turbulent water systems at ordinary pressures.

(6) A logical explanation of the numerical magnitude of the above gas exchange ratios in terms of the size of the gas molecules can be obtained from consideration of Einstein's basic law of diffusion. The derived relationship is:

$$\frac{K_1}{K_2} = \frac{d_2}{d_1} \qquad (4)$$

where the subscripts identify the two gases involved, K is the gas exchange coefficient, and d is the diameter of the gas molecule. It was also noted that the available data of

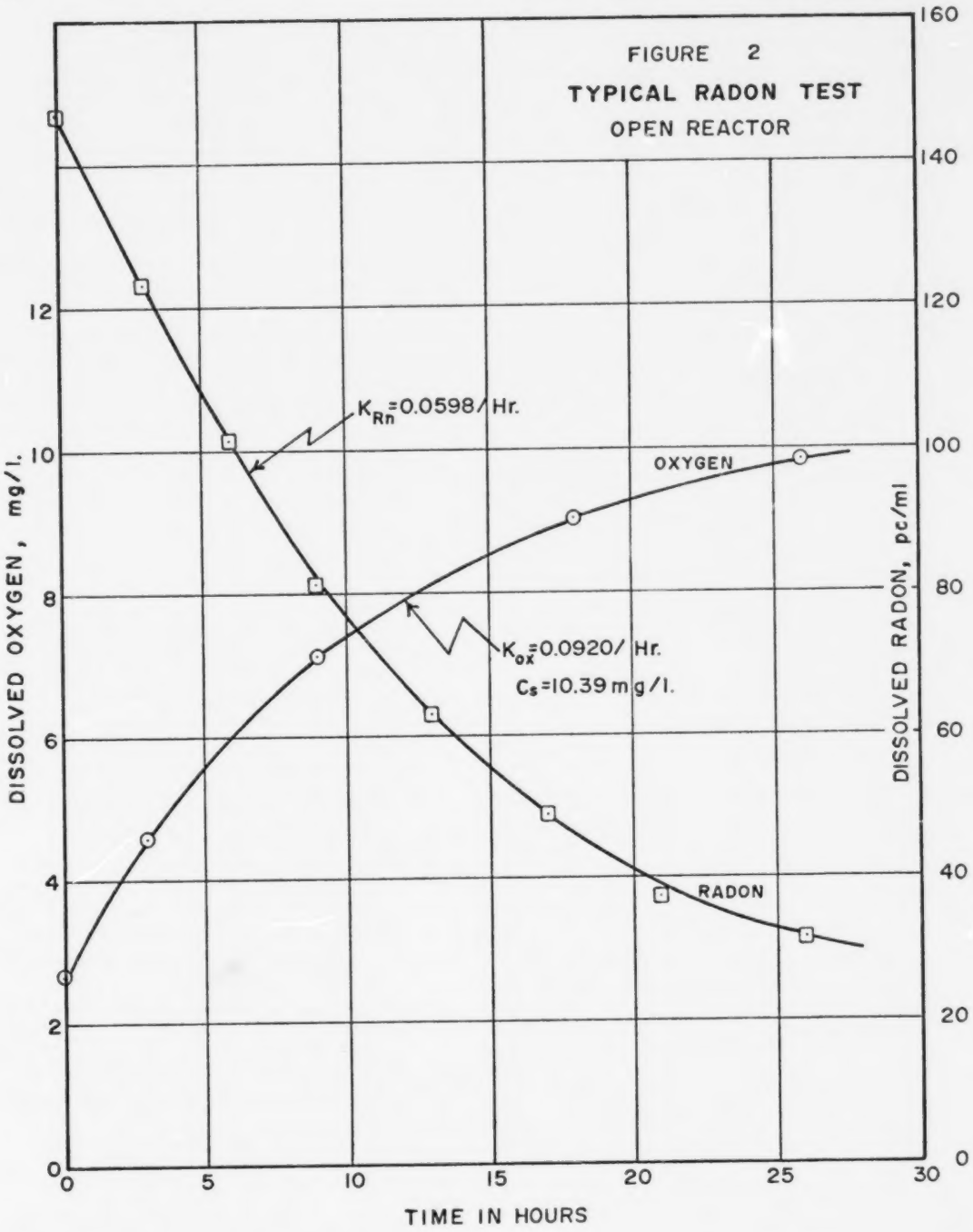


FIGURE 2
TYPICAL RADON TEST
OPEN REACTOR
K_{Rn}=0.0598/ Hr.
K_{ox}=0.0920/ Hr.
C_s=10.39 mg/l.
OXYGEN
RADON
DISSOLVED OXYGEN, mg/l.
DISSOLVED RADON, pc/ml
TIME IN HOURS
0
2
4
6
8
10
12
0
20
40
60
80
100
120
140
160
0
5
10
15
20
25
30

others on the diffusivity of various gases is in good agreement with the above relationship.

The foregoing experiments thus demonstrated the practical feasibility of using a tracer gas for independent evaluation of reaeration of natural rivers, and provided important insight as well regarding the nature of the gas exchange process in turbulent water systems. Certain specific questions remained unanswered by these open reactor tests, and led to the design and construction of an entirely different experimental system, described below. In particular, such questions involved the quality of the turbulent water surface (smooth, rippled, or broken) and the specific direction of gas transfer, and whether these factors might have any significant effect on the relative exchange abilities of the gases tested. In order to investigate such questions, and in order to further study the relationship between gas exchange and molecular diameter, it was necessary to extend the experiments to include other gases, and to provide for some variety of exchange surfaces and directions of gas transfer. The open reactor used in the early experiments could not be adapted to studies with other nonradioactive gases such as hydrogen, helium and nitrogen, as suitable and adequate methods for measuring the water concentrations of these gases were not available. Accordingly, a new gas exchange reactor was designed and utilized for experiments with these and other gases.

Carbon Dioxide-Oxygen Tests.—A later series of tests was conducted in the open reactor using carbon-14-labeled carbon dioxide gas with oxygen in distilled water, at temperatures that ranged from 22.2° C. to 32.3° C. (As indicated by Hutchinson and Sherwood [3] and by others, at such temperatures the amount of dissolved carbon dioxide that is involved in a chemical reaction with water is negligibly small.) As in the earlier tests with the open reactor, the initial concentration of D.O. was low (less than 1.0 mg/1) and the initial concentration of dissolved tracer gas was high, so that the concentration of the former increased with time during a test while the concentration of labeled dissolved carbon dioxide decreased with time. The concentration of labeled dissolved carbon dioxide was measured at regular intervals by counting replicate 2-ml water samples in a low background anticoincidence beta counter, and D.O. concentrations were followed by means of a D.O. probe and occasional Winkler determinations on discrete samples. Analysis of the resulting data for the two reaction rate constants and for the D.O. saturation limit approached was by the same techniques described in the earlier paper in re the radon-oxygen tests, except that radioactive decay of the carbon-14 was insignificant. The results of these tests are contained in Table I.

Referring to Table I, the mean exchange ratio for carbon dioxide and oxygen respectively was 0.894, with a range of 0.845 to 0.940, and a standard deviation of 0.034. The D.O. concentration in these tests approached a limiting value, on the average, of 94 percent of the Standard Methods value, just as in the earlier open reactor tests with krypton and radon. The probable reasons for this apparent 5 or 6 percent discrepancy have already been discussed,[6] and it has been concluded that it is quite unlikely that this apparent discrepancy is reflected in the numerical values of the derived gas exchange ratios.

TABLE I.—Carbon dioxide-oxygen tests

Temperature °C.	K_2/hr			c_s, mg/l		
	Carbon dioxide	Oxygen	CO_2/O_2	Observed	Standard Methods	Obs/St. M
31.4	0.427	0.485	0.881	6.80	7.18	0.947
28.9	0.314	0.369	0.852	7.15	7.63	0.938
22.2	0.120	0.131	0.917	8.14	8.64	0.943
22.8	0.054	0.061	0.885	7.91	8.56	0.925
23.5	0.148	0.160	0.925	8.06	8.40	0.960
22.5	0.153	0.177	0.865	7.71	8.55	0.902
23.5	0.120	0.128	0.938	7.53	8.34	0.903
22.5	0.064	0.068	0.940	8.50	8.53	0.996
23.7	0.152	0.174	0.873	7.87	8.37	0.940
29.9	0.207	0.226	0.916	7.36	7.61	0.968
32.3	0.317	0.375	0.845	6.52	7.25	0.900

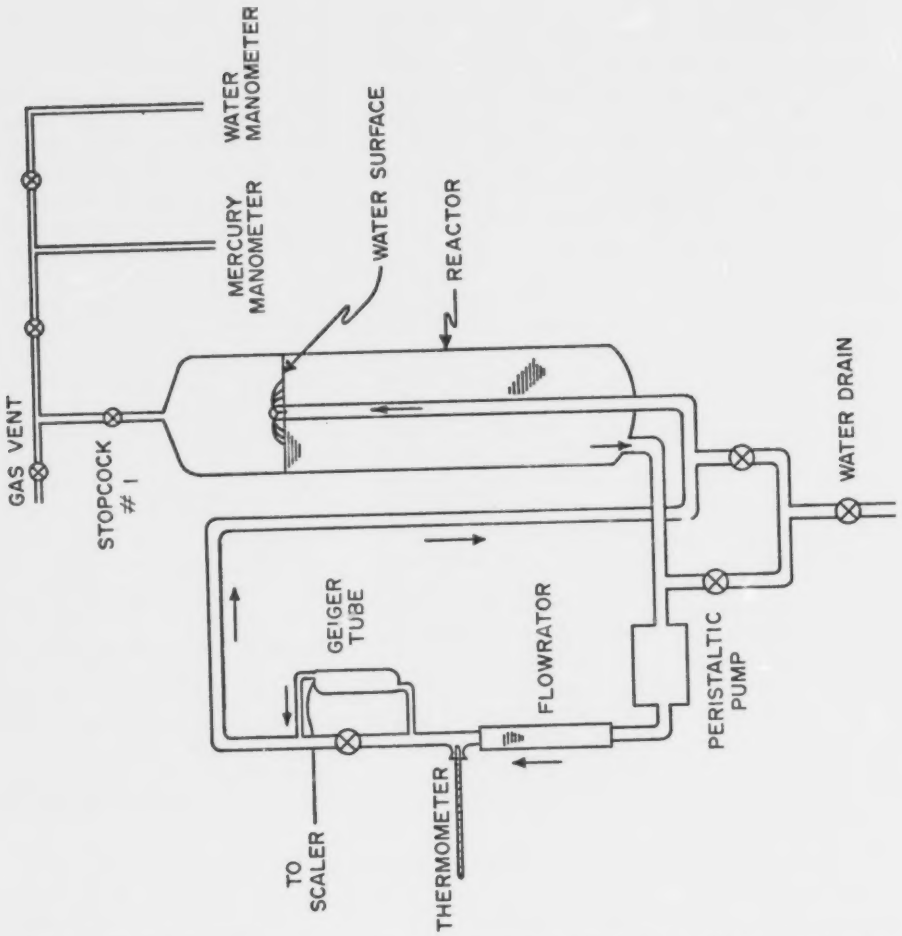


FIGURE 3
REACTOR II
SCHEMATIC

CONSTANT VOLUME REACTOR TESTS

Reactor II (see Fig. 3) is a recirculating water system for experiments using trace quantities of krypton-85 in pure carrier gases such as those noted above. Initially, the reactor is filled with thoroughly degassified water to a predetermined level; the space above the water surface is filled with a measured amount of the test gas (hydrogen, etc.) containing a trace quantity of krypton-85; the experiment consists of observing the simultaneous uptake of both gases by the water at a fixed recirculation rate and temperature. Uptake of the test gas by the water is evaluated in terms of the manometric pressure changes that are observed on the Hg and/or water manometers. The rate at which the tracer gas becomes dissolved in the water is evaluated in terms of the radioactivity measurements made with the flow-through Geiger tube, as in the earlier experiments with Reactor I. The quantity of krypton-85 present in the system is entirely negligible so far as effects on the observed pressure changes are concerned. The typical experiment consisted of continuing the

observations of radioactivity of the water and manometric pressure changes until the steady state condition was closely approached. This permitted analysis of virtually the entire course of the possible reaction for the desired reaction rate constants, as well as providing for separate verification of the test in terms of the known solubility of the test gas.

Reactor II was an all glass system, except for the tubing associated with the peristaltic pump. The reactor was completely contained in an external water bath for purposes of maintaining a constant water temperature. The total volume of the gas exchange system, including the reactor, the pump, and the flow-through Geiger tube and all tubing, but exclusive of the manometer capillary tubing beyond stopcock No. 1 (see drawing), was 5.34 liters. The gas volume from stopcock No. 1 to the Hg manometer was 16 ml, whereas the gas volume from the same point to the water manometer was 26 ml.

Operation of the Constant Volume Reactor

Referring to Figure 3, the test water is pumped out of the reactor via the bottom outlet, then passes through the pump tubing, a flowrator, and past a thermometer; a portion of the flow is then diverted through the jacket surrounding the flow-through Geiger tube and subsequently rejoins the main flow, which passes back into the reactor through the central glass column, to be discharged into the reactor at or near the water surface. The glass column has several peripheral slit openings at the top, so that water is released into the reactor at all sides. Stopcocks leading to the desired manometer are open, so that pressure changes can be observed. Thus, for any experiment, the recirculation rate and temperature are fixed and the volume of test water is constant. As the test gas dissolves into the water, the gas pressure drops systematically toward an equilibrium condition, while the radioactivity of the test water increases toward its own asymptotic limit as the krypton-85 becomes dissolved. Flows and temperatures are also recorded during the test. The resulting pressure and radioactivity data are analyzed for the respective reaction rate constants and for the observed solubility of the test gas.

For a fixed recirculation rate, the rate of the gas exchange reaction could be adjusted initially as desired for any particular experiment by means of the level to which the reactor was filled with test water. The slit openings at the top of the glass inlet column could thus be fully submerged by the test water for relatively slow reactions with an unbroken surface, or the openings could be fully exposed to provide for fast reactions by permitting the test water to enter freely and to splash onto the sides of the reactor and the water surface. Intermediate surface conditions and reaction rates could be obtained by suitable presetting of the water surface level. This permitted experiments of quite short duration (less than 1 hour) as well as longer tests ranging up to 16 hours in duration, and thus provided for a substantial range of observation. In particular, this design provided for a wide variety of water surface conditions, from quite smooth surfaces without apparent rippling to fully broken surfaces.

It should be noted also that the direction of transfer of the gases in these tests is different from those in which Reactor I was used. In experiments with Reactor I, the oxygen transfer was from the atmosphere into the test water, and the krypton-85 transfer was from the test water to the atmosphere. In the experiments with Reactor II, both the test gas and the tracer gas were transferred from the gas atmosphere into the test water.

Initial Test Conditions.—In the typical experiment, the reactor was initially completely evacuated, and then permitted to fill completely with test water through the water valve system. The test water was distilled water that had previously been boiled for several hours under a vacuum so as to rid it of all gases. (During the process of filling the reactor, triplicate Winkler D.O. determinations were made on the test water as one means of testing the quality of the water; commonly, there was an apparent 0.1 or 0.2 mg/1 of D.O. present.) A predetermined quantity of test water was then allowed to flow back out of the system, with stopcock No. 1 open to the room atmosphere. The resulting space above the water was then thoroughly evacuated to remove the air, to the extent of briefly boiling the water under vacuum. The test gas, containing a trace amount of krypton-85, was then introduced at the top from a supply tank through the gas vent and stopcock #1. The system was brought to a pressure slightly greater than atmospheric, manometer levels noted, and other required adjustments made, and the pump was then started to begin the experiment. After each experiment the entire system was drained using appropriate valves, and final Winkler dissolved oxygen tests were conducted on the test water as one means of testing for any possibility of an air leak into the system during the test.

The entire system was tested frequently for gas leaks by submitting it to overnight tests in which it was required to hold either a full vacuum or a gas pressure substantially greater than atmospheric. Such tests were especially important during the hydrogen and helium series of experiments, as these gases are notorious for their ability to leak out of apparently tight experimental systems. Thus the ability of the reactor system to hold an overpressure of these gases overnight without detectable pressure change was verified frequently during the series of experiments with hydrogen and helium.

All of the tests for relative gas exchange capability performed in Reactor II were conducted at 20° C., as the earlier tests with the open reactor had indicated no significant temperature effect on the gas exchange ratios within the temperature range of interest.

Theoretical Basis

The course of the gas exchange reactions that take place in the constant volume test system described above and shown in Figure 3 is outlined in the following mathematical developments.

Consider the initial experimental situation, in which the test water level in the reactor has been preset, a measured volume of test gas has been introduced into the reactor space above the water surface, initial gas pressure in the system has been fixed by means of appropriate stopcocks and valves, and recirculation of the degassified test water has just been started; let

$c_{gw}(t)$ be the concentration of test gas in the test water at time, t, in mg/l.

$c_s(t)$ be the momentary (transient) saturation limit of the test gas in the test water at time, t, in mg/l. This is the concentration of test gas that we would have in the test water at time, t, if $c_{gw}(t)$ were the value obtained from Henry's Law corresponding to the pressure of test gas in the space above the water surface.

$c_s(0)$ is therefore the saturation limit of the test gas in the test water at time $t=0$, before gas transfer has started.

$c_{gw}(\infty)=c_s(\infty)$ is the concentration of test gas in the test water that will be approached as time approaches infinity.

Referring to Figure 4, the gas transfer process that takes place can be described in terms of the change of $c_{gw}(t)$ with time, in terms of the change of $c_s(t)$ with time, and in terms of the change of the difference $[c_s(t)-c_{gw}(t)]$ with time. Thus three distinct differential equations can be written to describe the reaction as follows:

$$\frac{dc}{dt}gw^{(t)}=K_2\{c_s(t)-c_{gw}(t)\} \qquad (5)$$

$$\frac{dc}{dt}s^{(t)}=-K_s\{c_s(t)-c_{gw}(t)\} \qquad (6)$$

$$\frac{d}{dt}\{c_s(t)-c_{gw}(t)\}=-K_g\{c_s(t)-c_{gw}(t)\} \qquad (7)$$

Analysis of these equations indicates that the three proportionality constants are not the same, but are related by the expression:

$$K_g=K_s+K_2 \qquad (8)$$

To summarize, K_2 is the desired rate constant for the increasing concentration of test gas in the test water; K_s refers to the speed with which $c_s(\infty)$ is approached, or to the rate of change of the equilibrium gas pressure; K_g is the rate constant for the decrease of the saturation deficit with time. For the constant volume experimental system with which we are concerned, equation (7) above reflects the course of the observed reactions. From this, the K_g's can be evaluated for each experiment, and converted to the desired K_2's reflecting the rate of change of $c_{gw}(t)$, by means of the expressions developed below.

In general

$$N_{gw}(t)=\frac{c_{gw}(t)V_w\times 10^{-3}}{M_g} \qquad (9)$$

where $N_{gw}(t)$ is the number of moles of gas dissolved in the water, at time t,

V_w is the volume of water, in liters, and

M_g is the molecular weight of the gas.

Also, $c_s(t)$ corresponds to the momentary value of $p_g(t)$ according to Henry's Law, so that

$$P_g(t)=k_H\frac{N_{gw}(t)}{N_w}=\frac{k_H}{N_w}\{c_s(t)\frac{V_w}{M_g}\times 10^{-3}\} \qquad (10)$$

where

$p_g(t)$ is the pressure of the test gas in the space above the water, in mm of H_g,

k_H is Henry's constant for the test gas, in mm/mole fraction,

and

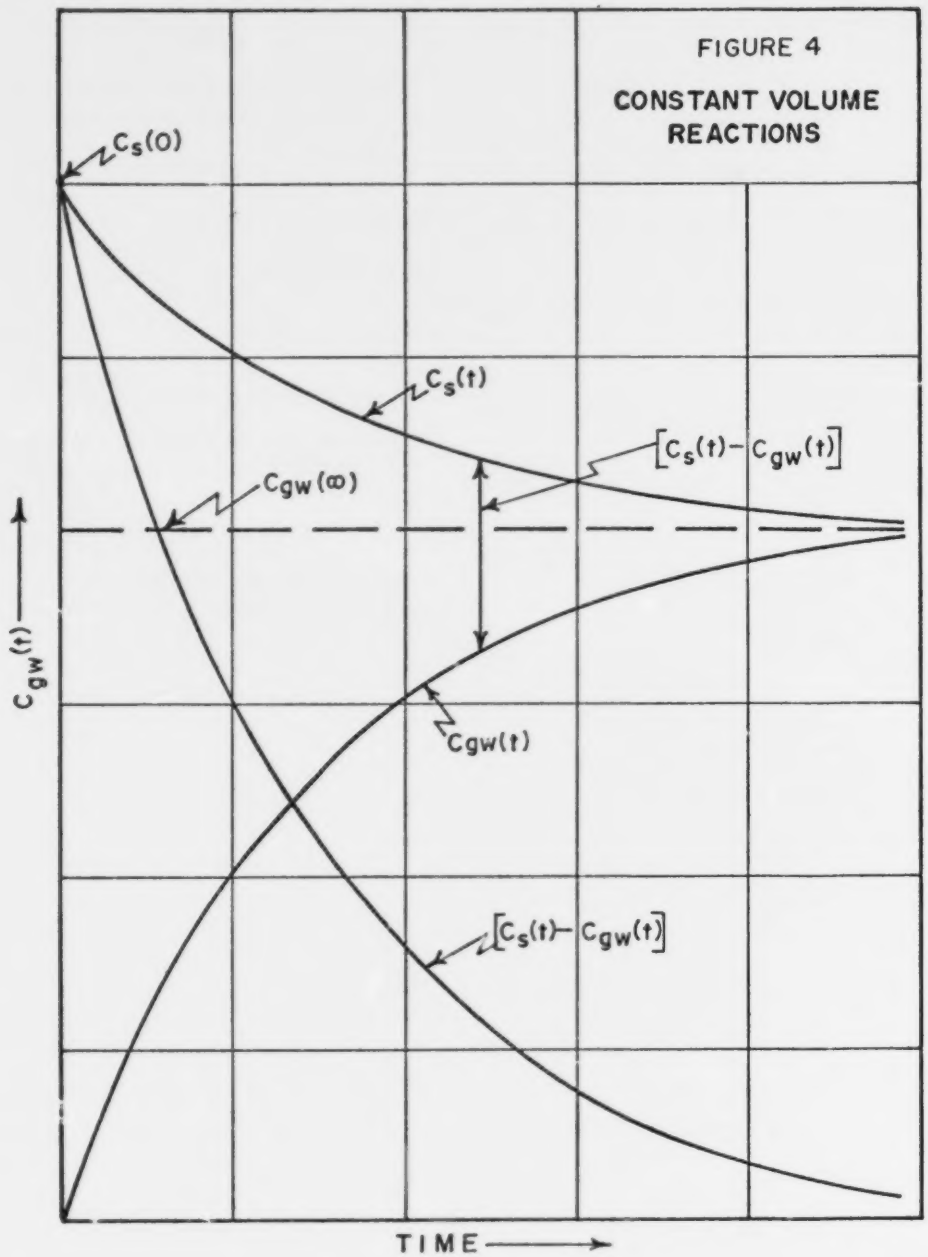
N_w is the number of moles of water.

Also, by the ideal gas law

$$P_g(t)=\frac{760RTN_g(t)}{V_g} \qquad (11)$$

where

V_g is the volume of the gas space, in liters,



$N_g(t)$ is the number of moles of undissolved test gas at time t,
T is the absolute temperature, ° K, and
R is the universal gas constant in liter-atm/mole ° K.

And, finally

$$N_{gw}(t) = \{N_{og} - N_g(t)\} \qquad (12)$$

where

N_{og} = the number of moles of test gas initially present in the space above the water.

Combining these equations and rearranging terms lead to

$$\{c_s(t) - c_{gw}(t)\} = \frac{M_g}{10^{-3}V_w}\{(\frac{760RTN_w}{k_{11}V_g} + 1)N_g(t) - N_{og}\}, \quad (13)$$

and this form will be used in the following developments.

Derivation for K_2. Referring now to equation (5)

$$\frac{dc_{gw}(t)}{dt} = K_2\{c_s(t) - c_{gw}(t)\} \quad (5)$$

it is readily shown that

$$\frac{dc_{gw}(t)}{dt} = -\frac{M_g}{10^{-3}V_w}\frac{dN_g(t)}{dt} \quad (14)$$

by the use of equations (9) and (12). Now, by the use of equations (13) and (14) in equation (5), and letting

$$A = \frac{k_{11}V_g}{760RTN_w} \quad (15)$$

it follows that

$$\frac{dN_g(t)}{dt} = -K_2(\frac{1+A}{A})N_g(t) + K_2N_{og} \quad (16)$$

Solving, we obtain

$$N_g(t) = (\frac{A}{1+A})N_{og} + (\frac{1}{1+A})N_{og}e^{-K_2(\frac{1+A}{A})t} \quad (17)$$

and, using (12),

$$N_{gw}(t) = (\frac{A}{1+A})N_{og}\{1 - e^{-K_2(\frac{1+A}{A})t}\} \quad (18)$$

Derivation for K_g. Referring to equation (7)

$$\frac{d}{dt}\{c_s(t) - c_{gw}(t)\} = -K_g\{c_s(t) - c_{gw}(t)\} \quad (7)$$

and using equations (13) and (15), it can be shown that

$$\frac{dN_g(t)}{dt} = -K_gN_g(t) + (\frac{A}{1+A})K_gN_{og} \quad (19)$$

which is solved by

$$N_g(t) = (\frac{A}{1+A})N_{og} + (\frac{1}{1+A})N_{og}e^{-K_gt} \quad (20)$$

Using (12) it also then follows that

$$N_{gw}(t) = (\frac{1}{1+A})N_{og}\{1 - e^{K_gt}\} \quad (21)$$

Comparison now of equations (18) and (21) yields

$$K_g = K_2(\frac{1+A}{A}) \quad (22)$$

Derivation for K_s. Using equations (6), (10), (11), (13), and (15) it can be demonstrated that

$$\frac{dN_g(t)}{dt} = -K_s(1+A)N_g(t) + K_sAN_{og} \quad (23)$$

The solution to (23) is

$$N_g(t) = (\frac{A}{1+A})N_{og} + (\frac{1}{1+A})N_{og}e^{-K_s(1+A)t} \quad (24)$$

whence, by (12)

$$N_{gw}(t) = (\frac{1}{1+A})N_{og}\{1 - e^{-K_s(1+A)t}\} \quad (25)$$

Comparison now of equations (18), (21), and (25) indicates by inspection that

$$K_s(1+A) = K_g = K_2(\frac{1+A}{A}), \quad (26)$$

and this agrees with equation (8).

From the foregoing solutions it is also evident that

$$N_g(\infty) = (\frac{A}{1+A})N_{og} \quad (27)$$

and that

$$N_{gw}(\infty) = (\frac{1}{1+A})N_{og} \quad (28)$$

Analysis of Observed Data—Typical Example

For any individual test, it is desired to calculate the observed exchange coefficients for the test and tracer gases, and the ratio of the two coefficients. As general verification, it is desired also to compare the observed solubility of the test gas with the expected Henry's Law solubility. The absorption of test gas by the water is reflected by the observed systematic change of pressure in the space above the water. Uptake of the tracer gas by the water is indicated by the Geiger tube measurements of radioactivity.

For any specific test, the reactions of equations (18), (21), and (25) are first order, and lend themselves to graphical solution. Test No. 49, in which the test gas was oxygen, was typical, and will serve as an example for illustration of the analysis of the observed data. Figures 5 through 8 show the observed experimental data and the methods of analysis for the gas exchange coefficients.

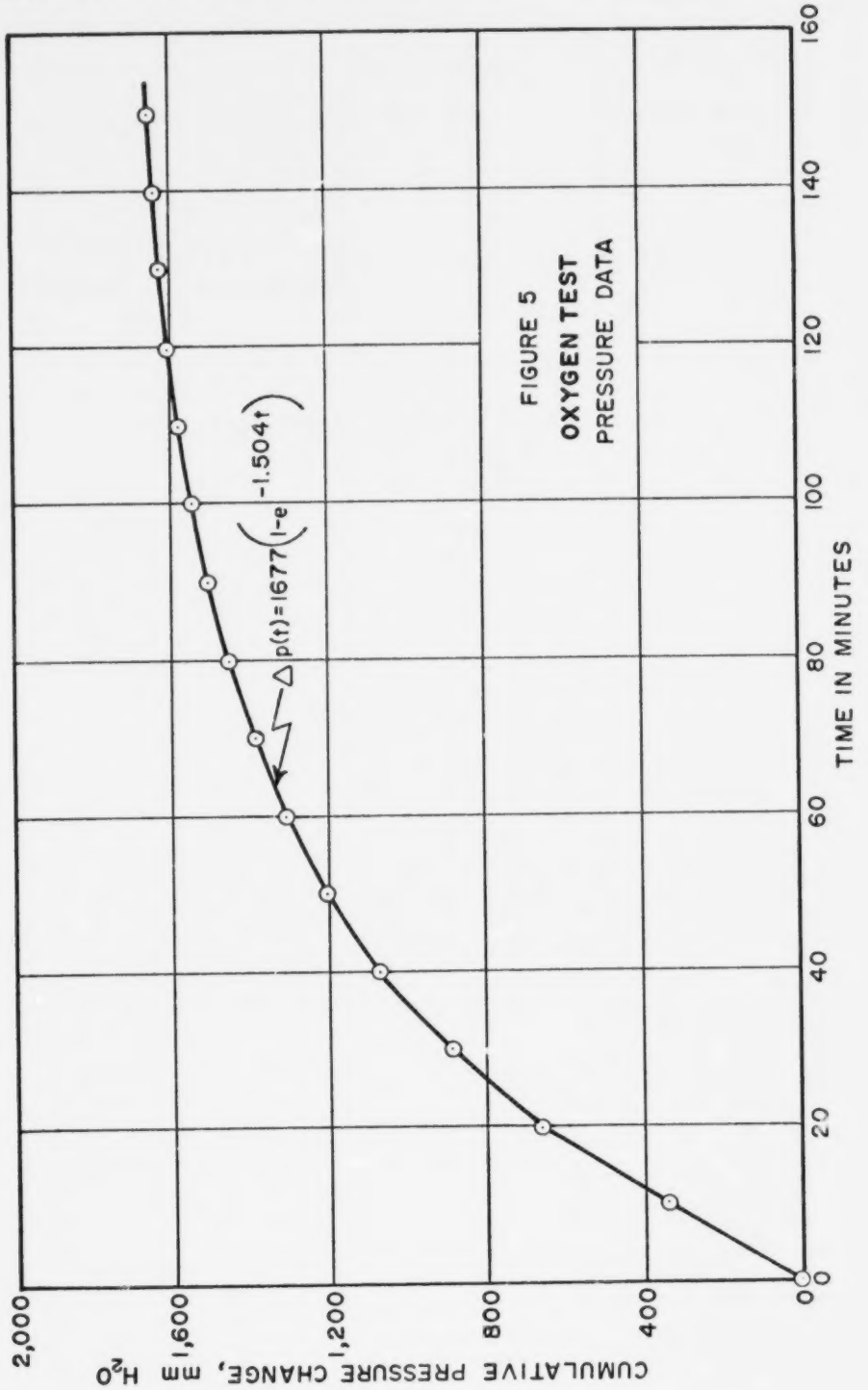
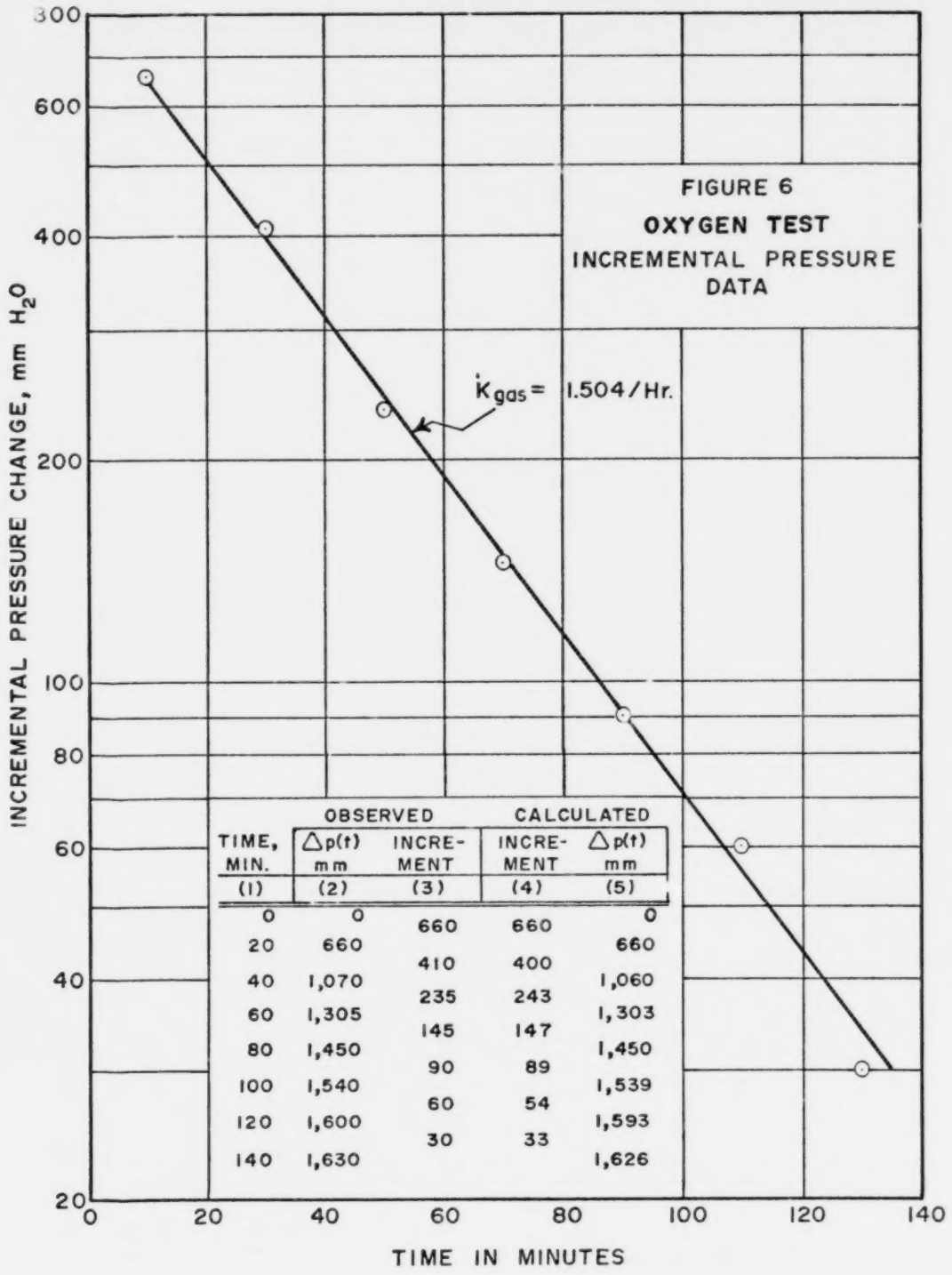


FIGURE 5
OXYGEN TEST
PRESSURE DATA
Δp(t)=1677(1-e^-1.504t)
CUMULATIVE PRESSURE CHANGE, mm H2O
TIME IN MINUTES
0
400
800
1,200
1,600
2,000
0
20
40
60
80
100
120
140
160



TIME, MIN.	OBSERVED Δp(t) mm	OBSERVED INCREMENT	CALCULATED INCREMENT	CALCULATED Δp(t) mm
(1)	(2)	(3)	(4)	(5)
0	0	660	660	0
20	660	410	400	660
40	1,070	235	243	1,060
60	1,305	145	147	1,303
80	1,450	90	89	1,450
100	1,540	60	54	1,539
120	1,600	30	33	1,593
140	1,630			1,626

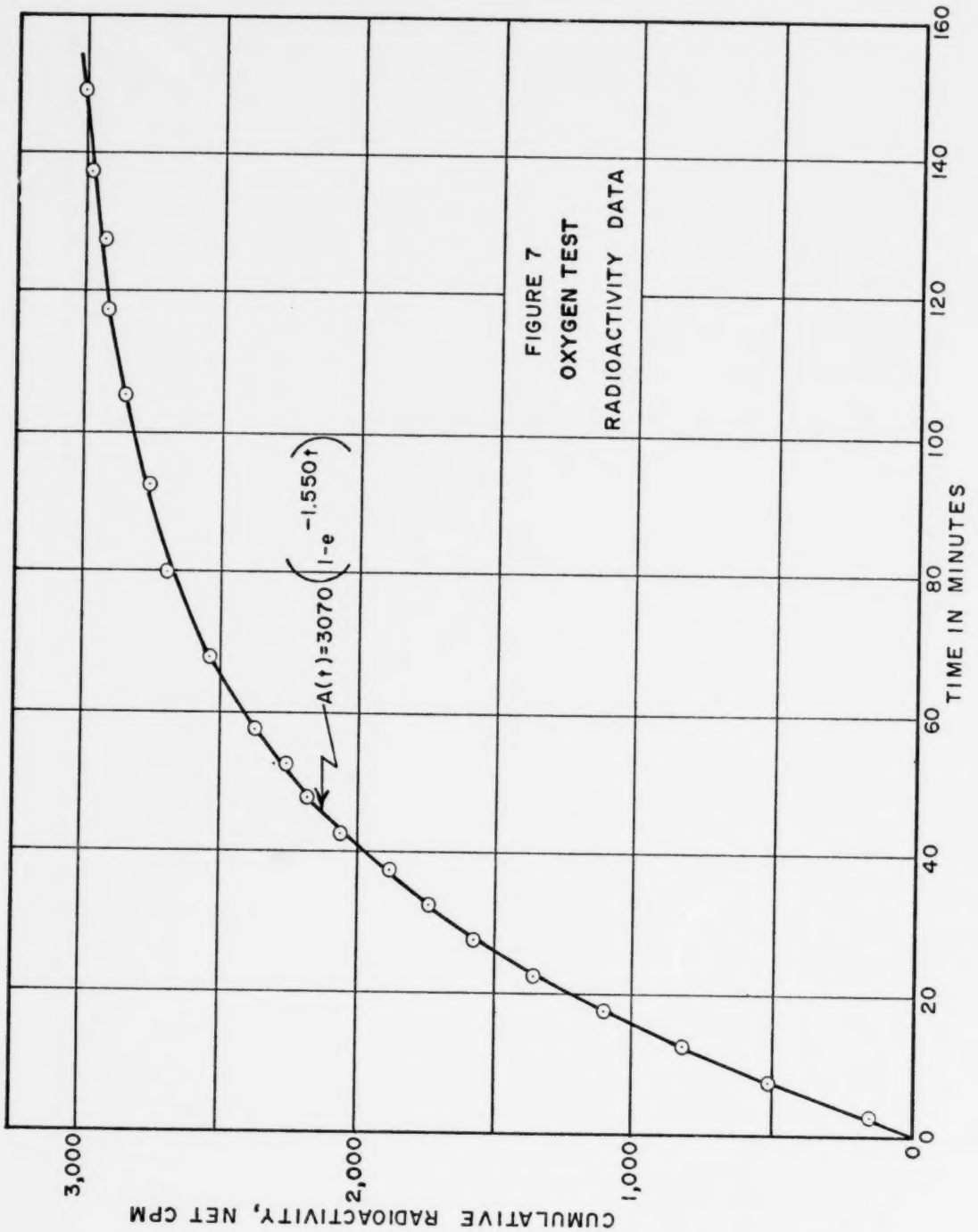


FIGURE 7
OXYGEN TEST
RADIOACTIVITY DATA
A(t)=3070 (1-e^-1.550t)
CUMULATIVE RADIOACTIVITY, NET CPM
TIME IN MINUTES
0
1,000
2,000
3,000
0
20
40
60
80
100
120
140
160

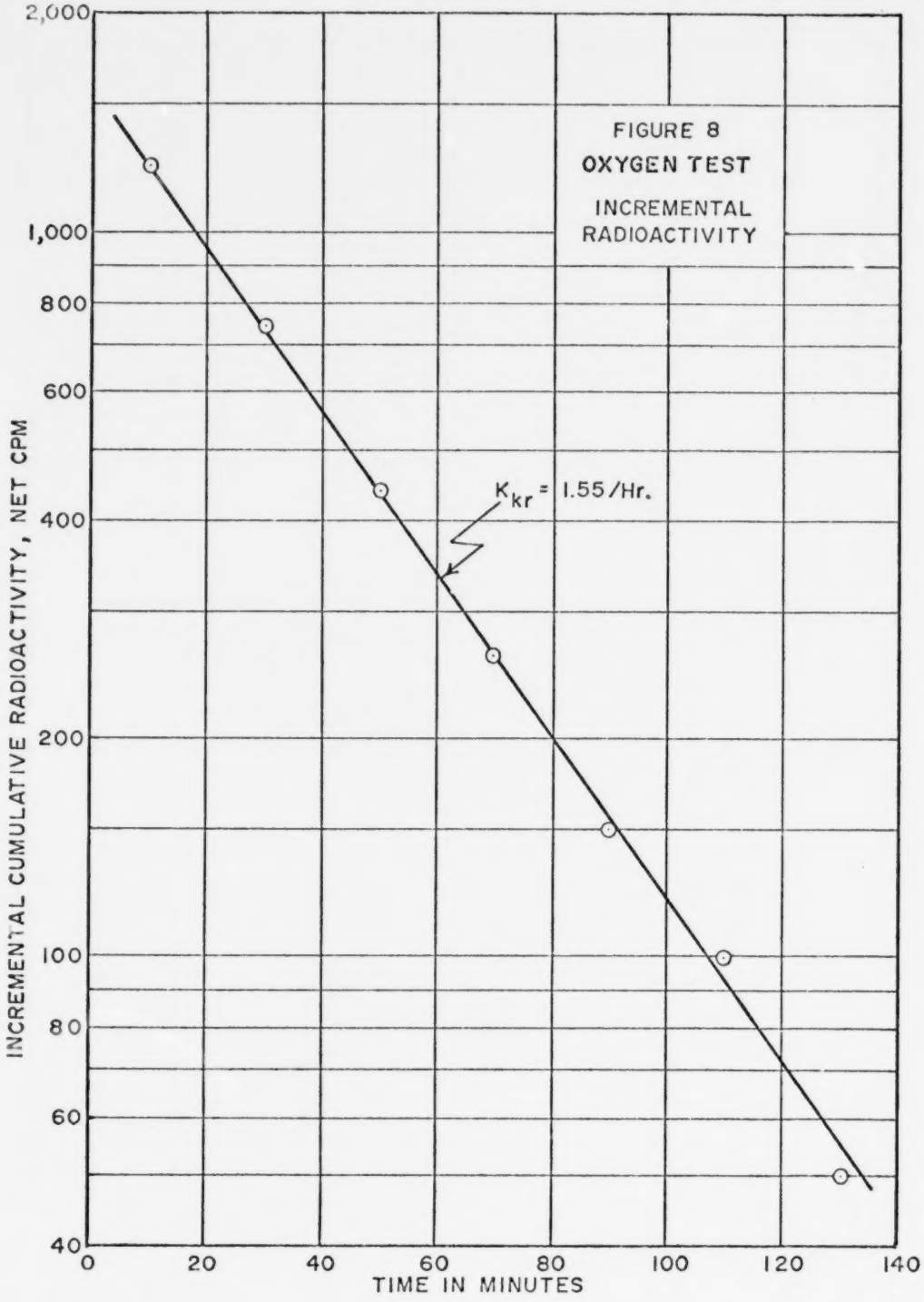


FIGURE 8
OXYGEN TEST
INCREMENTAL
RADIOACTIVITY
K_{kr} = 1.55/Hr.
INCREMENTAL CUMULATIVE RADIOACTIVITY, NET CPM
2,000
1,000
800
600
400
200
100
80
60
40
0
20
40
60
80
100
120
140
TIME IN MINUTES

Test Gas Reaction Kinetics.—Figure 5 is a graph of the observed change of pressure in the gas space, as indicated by the manometer readings, versus duration of the test in minutes. (The common experimental practice was to begin the test with a slight overpressure of test gas, hence at an early stage of the test the manometer went through a zero pressure difference. In this case, test number 49, the initial overpressure was unusually small, only 3 mm. on the water manometer, and so is not easily seen in Fig. 5.) The smooth curve drawn through the observed data is the calculated first order reaction curve fitted by the graphical procedure shown in Figure 6.

The observed changes in gas pressure over equal intervals of time were used for the analysis shown in Figure 6. In the example, equal 20-minute intervals were used. For a first order reaction, the incremental pressure changes for equal time intervals should plot as a straight line on semilog paper, the slope of the line being the reaction rate constant. Referring to Figure 6, the observed incremental pressure changes for 20-minute time intervals were obtained from the observed data (see tabulation, col. 3), and were plotted versus time. A straight line was fitted to these data, and, as may be seen, described the course of the reaction excellently throughout its entire duration. Referring now to equation (21), it is seen that the slope of the straight line is the observed value of K_g for the test gas in this experiment. In the case of test number 49, the numerical value of K_g thus obtained was 1.504/hour.

Construction of the calculated smooth curve of Figure 5, and consequent verification of the analysis of Figure 6, is most readily performed from figure 6. Referring to Figure 6, the calculated incremental pressure changes are obtained by reading them directly from the fitted straight line, and are tabulated in column (4). These increments are then accumulated to yield the cumulative pressure changes. These are recorded in column (5) of Figure 6, and represent the calculated results plotted as the smooth curve through the observed data of Figure 5.

The limiting value of the curve of Figure 5 is also obtained directly from Figure 6. In the case shown, the calculated cumulative pressure change of 1593 mm. H_2O after two hours is divided by

$$\{1-e^{-(1.504)(2.0)}\}=0.9505$$

to yield a result of 1677 mm. H_2O for the limiting cumulative pressure change, or the result approached at infinite time.

Thus in the example shown, the test gas exchange reaction was observed experimentally throughout about 97 percent of its full extent. As may be seen from Figures 5 and 6, the reaction is first order, and the observed data are fitted very closely throughout the course of the test by the calculated curve. This was typical of all of the test runs with the several gases used in Reactor II.

The reaction rate constant desired is K_2, rather than the observed K_g obtained above. Reference to equation (26) above indicates that

$$K_2=\left(\frac{A}{1+A}\right)K_g,$$

and the constant A is evaluated for any test by means of the relationship

$$A=\frac{k_H V_g}{760RTN_w} \qquad (15)$$

defined earlier, which is a function of the specific gas (Henry's constant, k_H, being specific for each gas), and of the specific gas-to-liquid volume ratio for any specific test. The numerical value of K_2 for the test gas in any experiment is thus obtained by first evaluating the test constant, A, and then evaluating K_2 by use of A and the observed K_g. For experiment number 49, using oxygen, the gas-to-liquid volume ratio was 0.1530, and Henry's constant $=3.04\times10^7$ mm. Hg per mole fraction at 20° C. Thus the value of A is 4.58 for oxygen in this test, and using the observed K_g of 1.504/hr., the value of K_2 for oxygen is found to be

$$(K_2)_{ox}=\frac{4.58}{5.58}(1.504)=1.236/\text{hr.}$$

Test Gas Solubility.—The observed changes of pressure in the gas space over the water in Reactor II throughout the course of any specific experiment are a direct reflection of the solubility of the test gas in water. Thus, comparison of the observed gas solubility with that expected on the basis of Henry's Law provides an important general test of the validity of the entire experiment and its inherent assumptions, and also yields a very useful measure of the maximum possible degree of error in the experimental results. Experiment number 49 will serve below as an example of these calculations and their interpretation.

As shown above, the limiting, or infinite time, cumulative observed pressure change in test number 49 was 1677 mm. on the water manometer. This corresponds to an observed pressure change of 123.8 mm. Hg (Specific gravity of Hg = 13.55 gm/cc.). The initial gas over-pressure in this case

was only 3 mm. H_2O, or 0.2 mm. Hg. Thus, the total observed pressure change was 124.0 mm. Hg.

Any change in barometric pressure during the experiment must also be accounted for, as one side of the manometer is open to the atmosphere. In the vast majority of tests this change in barometric pressure was quite small (1 or 2 mm. Hg) and no correction of the test data was required for purposes of calculating the reaction rate constant. In about one case out of 10, the barometric pressure change was larger (3 to 5 mm. Hg), and in such cases the individual observed pressure changes during test were corrected on the basis of the corresponding observed barometric pressures before the analysis for K_g. For experiment number 49, the barometric pressure dropped 0.4 mm. Hg during the course of the test, the observed barometric pressure at the end of the test being 732.1 mm. Hg. The true total pressure change for test number 49 was therefore 124.0+0.4, or 124.4 mm. Hg.

Using the ideal gas law, together with equation (9), it is readily shown that

$$c_{gw}(\infty) = \frac{\Delta P_g(\infty) V_g M_g}{0.760\ RTV_w} \qquad (29)$$

where $c_{gw}(\infty)$ is the concentration of test gas in solution at time infinity, in mg/1,

$\Delta p_g\ (\infty)$ is the true total pressure change, in mm. Hg,

M_g is the molecular weight of the gas, in gm/mole,

V_g is the volume of gas, in liters,

V_w is the volume of test water, in liters,

R is the universal gas constant, in liter-atm/mole ° K, and

T is the temperature, in ° K.

For test number 49, calculation according to equation (29) indicates that, based upon the observed true pressure changes, the concentration of oxygen dissolved in the water that would have been attained at infinite time was 33.3 mg/1.

The concentration of dissolved oxygen that should have been reached at infinite time can be computed from Henry's Law. Using Henry's Law together with equation (9), it is found that

$$c^H_{gw}(\infty) = \frac{P_g(\infty) M_g \times 10^6}{18 k_H} \qquad (30)$$

where

$c^H_{gw}(\infty)$ is the Henry's Law oxygen concentration in the test water at infinite time, in mg/1, corresponding to $P_g(\infty)$, and

$P_g(\infty)$ is the pressure of the test gas in V_g at infinite time, in mm. Hg.

The pressure of the test gas, $p_g(\infty)$, in V_g at infinite time is just the observed final barometric pressure, $(p_{bar})_f$, minus the observed pressure difference corresponding to $t=\infty$, and minus 17.5 mm. Hg, which is the vapor pressure of water in the reactor. Thus for experiment number 49

$P_g(\infty) = 732.1 - 123.8 - 17.5 = 590.8$ mm. Hg.

Using this numerical result, together with $k_H = 3.04 \times 10^7$ mm/mole fraction for oxygen, in equation (30), it is found that the Henry's Law dissolved oxygen concentration at time infinity is 34.6 mg/1.

Thus, the comparison of observed versus expected gas solubility indicates for test number 49 that

$$\frac{33.3}{34.6} = 0.963,$$

or that the observed dissolved oxygen concentration reached 96.3 percent of the expected concentration. This result is fairly typical of all of the tests, as will be seen later in the tabulations of test results.

The sources of experimental error that might lead to results such as this are discussed in some detail at a later point, and provide the probable explanation of the slightly low observed result. However, the magnitude of the discrepancy is the significant matter, as it provides a valid measure of the extent of possible error in the derived gas exchange capability ratios. It is evident that, even if the above discrepancy were real and were directly reflected as a corresponding error in the observed oxygen K_2 of 1.236/hr., the possible extent of this error in the derived gas exchange ratios could only be quite small, and, in fact, insignificant for practical purposes. As will be seen, examination of the possible sources of error, together with all of the evidence provided by the test data, indicates that the discrepancy evaluated above was of a type that is not reflected as a corresponding error in the observed test gas transfer coefficients.

The solubility test shown above must be regarded as a very important general test of the validity of experiments such as those reported here. Without this general verification procedure, it is not possible to know the real range of error that may be associated with the test results, nor is it possible to be assured of the true course of the whole reaction. In particular, the solubility test is a vital requirement as a means of detecting

the presence of extraneous or unsuspected side reactions that may result in large or even gross error. For example, a gas leak in a system such as that described here, or in a similar constant pressure test system, might very well be first order, or nearly so, in nature. Without the solubility test, such a leak would most probably remain undetected and unsuspected. A second useful example is provided by the analysis of corrosive oxidation presented in the earlier paper on this work [6]—in that case, the solubility of oxygen test was the only means of detecting and evaluating the extraneous process.

As a final practical example of the importance of the solubility test, it is not at all uncommon for an investigator to limit his observations to two points on a curve similar to that of Figure 5, assume that the whole reaction was first order, and calculate the gas transfer coefficient by assuming that the handbook gas solubility limit was being approached. The gas transfer coefficient so calculated can only be regarded as an estimate, and not a measurement, as the several stated and implied assumptions are all subject to error, and certain of these potential errors are not small.

Tracer Gas Reaction Kinetics.—The concentration of the tracer gas, krypton-85, increases steadily throughout the course of each experiment, and is measured by the flow-through Geiger tube in terms of its radioactivity. Figure 7 shows, for test number 49, the observed radioactivity, in cumulative counts per minute (cpm) as a function of the duration of the test, in minutes. The radioactivity per unit volume also approaches a limiting value represented by the solubility of krypton-85 in the test water.

The radioactivity data are most readily analyzed by the graphical procedure already outlined for analysis of pressure changes. Figure 8 shows the semilog paper plot of the incremental increases of radioactivity versus time for experiment number 49. In this case, because the actual times of observation were slightly different, the observed data for equal 20-minute intervals were obtained by interpolation from the observed results. The resulting calculated curve is plotted on Figure 7, and fits the observed data excellently. The observed slope, K_g, of the straight line shown in Figure 8 was 1.550 per hour, and reference to equation (26) indicates therefore that

$$(K_2)_{Kr} = \left(\frac{A}{1+A}\right) \times (1.550).$$

Referring to equation (15), and using the Henry's Law Constant for krypton of 1.52×10^7 mm/mole fraction, it is found that for test number 49, the numerical value of A for krypton is 2.29, whence

$$(K_2)_{Kr} = \frac{(2.29)}{(3.29)} \times (1.550) = 1.079/\text{hr}.$$

As shown on Figure 8, the asymptotic limit approached by the cumulative radioactivity curve is 3,070 cpm.

Gas Transfer Ratio.—The relative gas transfer capability of the two gases, oxygen and krypton-85, is measured by the ratio of the K_2 values. For experiment number 49, the desired ratio is

$$\frac{(K_2)_{Kr}}{(K_2)_{ox}} = \frac{1.079}{1.236} = 0.873.$$

This ratio of exchange coefficients is dimensionless. Because it has been determined by simultaneous measurement of both gas transfer processes in a single turbulent water system, it is quite independent of the degree of turbulent mixing or the degree of agitation of the air-water interface. Even though turbulence does decidedly influence the magnitude of the individual K_2 values, the ratio is unaffected for any individual test. Thus, although the individual K_2 values may be regarded only as relative measurements, the ratio of K_2 values is of the nature of an absolute result.

The gas transfer reactions as reported in the following section were all analyzed by the procedures shown above. The solubility test that has been outlined was applied in each case for positive evaluation of the extent of possible error in the test gas exchange coefficients and as a means of providing positive assurance that no other unsuspected process (such as a gas leak, etc.) took place to any significant extent.

Experimental Results

A series of experiments similar to test number 49 was conducted using hydrogen, helium, nitrogen, oxygen and stable krypton as test gases, each together with trace quantities of krypton-85. All tests were conducted at 20° C. In all cases, Winkler D.O.'s were determined on triplicate samples of the test water, both at the beginning and at the end of the test, as one means of detecting any possible leaks of room air into the reactor, as well as for purposes of verifying the thoroughness of the initial degassification of the water. The individual gas transfer reactions were observed throughout about 95 percent of the course of the

possible reaction, and all of the observed reactions were verified as simple first order by the foregoing procedures.

Hydrogen-Krypton-85 Tests.—A total of seven reactor tests was conducted using the trace quantities of krypton-85 in pure hydrogen test gas. Figure 9, for test number 65, was typical of the results, and shows the observed reactor pressure changes and the observed cumulative radioactivity of the test water, together with the calculated first order reactions that fit the data. Table II contains the pertinent results for the seven tests.

TABLE II.—Hydrogen-krypton-85 tests, 20° C.

K_2/hr			Solubility of Hydrogen		
Krypton-85	Hydrogen	$\left(\frac{K_{Kr}}{K_{Hy}}\right)$	$c_{gw}(\infty)$, mg/l	$c^{H}{}_{gw}(\infty)$,* mg/l	$\left\{\frac{c_{gw}(\infty)}{c^{H}{}_{gw}(\infty)}\right\}$
2.50	4.21	0.593	1.39	1.42	0.979
2.23	3.74	0.595	1.33	1.42	0.937
1.83	3.12	0.588	1.39	1.42	0.979
1.31	2.24	0.585	1.33	1.44	0.923
0.927	1.50	0.617	1.30	1.39	0.935
0.600	1.07	0.561	1.35	1.34	1.007
0.149	0.263	0.565	1.12	1.24	0.903

*$k_H = 5.2 \times 10^7$ mm/mole fraction.

The range of observed gas exchange ratios was from 0.561 to 0.617, with an arithmetic mean of 0.586, and a standard deviation of 0.019. The median ratio was 0.588. The individual observed gas transfer coefficients (K_2/hr) for hydrogen ranged from 0.263 to 4.21 per hour.

Referring to the hydrogen solubility results, the observed final (infinite time) hydrogen concentration, $c_{gw}(\infty)$, ranged from 90.3 to 100.7 percent of the Henry's Law concentration, $c^{H}{}_{gw}(\infty)$, as shown in the last column of Table II. The mean value was 95.2 percent, indicating that, on the average, 95.2 percent of the Henry's Law solubility was achieved. The mean value of the initial D.O. determinations was 0.15 mg/1, and the mean observed final D.O. was 0.13 mg/1. Except for the oxygen-krypton-85 test series (see below), these D.O. results were typical. The sensitivity of the Winkler method at such a low oxygen concentration is questionable, and the best analytical laboratory technique is vital if zero D.O.'s are to be observed. Thus the apparent D.O. of 0.1 or 0.2 mg/1 is regarded as a real concentration of zero, and the above results indicate that the initial degassification of the test water was complete for practical purposes, and that no significant leak of outside air into the reactor occurred during these tests.

The failure to achieve the full Henry's Law solubility was typical also for the several test series, and is discussed in detail in the subsequent section of this chapter on sources of error. The difference between achieving 95.2 percent and 100 percent of the Henry's Law solubility represents a maximum possible error of the same order so far as the observed gas transfer coefficient is concerned, and such an error would be negligibly small from that viewpoint. However, as will be seen, analysis of the several possible sources of error indicates clearly that the kind of error involved would not detectably affect the observed gas transfer coefficient.

Helium-Krypton-85 Tests.—Seven constant volume reactor tests were performed using trace amounts of krypton-85 in pure helium test gas. As has been noted earlier, the reactor system was tested regularly between helium experiments in order to provide positive assurance that helium leaks would not occur during the tests. Figure 10, for test number 57, was typical. It shows the observed pressure and radioactivity changes during the test, with the calculated first order reactions that were fitted to the observed data. Table III contains the pertinent test results.

The observed gas exchange ratios ranged from 0.406 to 0.465, with an arithmetic average value of 0.438 and a standard deviation of 0.019. The median ratio was 0.438. The comparison between the observed and the Henry's Law solubilities indicated that the observed final helium concentration ranged from 93.6 to 104.3 percent of the Henry's Law result, with an average of 97.6 percent of the Henry's Law concentration achieved. The average initial D.O. for the helium tests was 0.25 mg/1, and the average final D.O. of the test water was 0.20 mg/1.

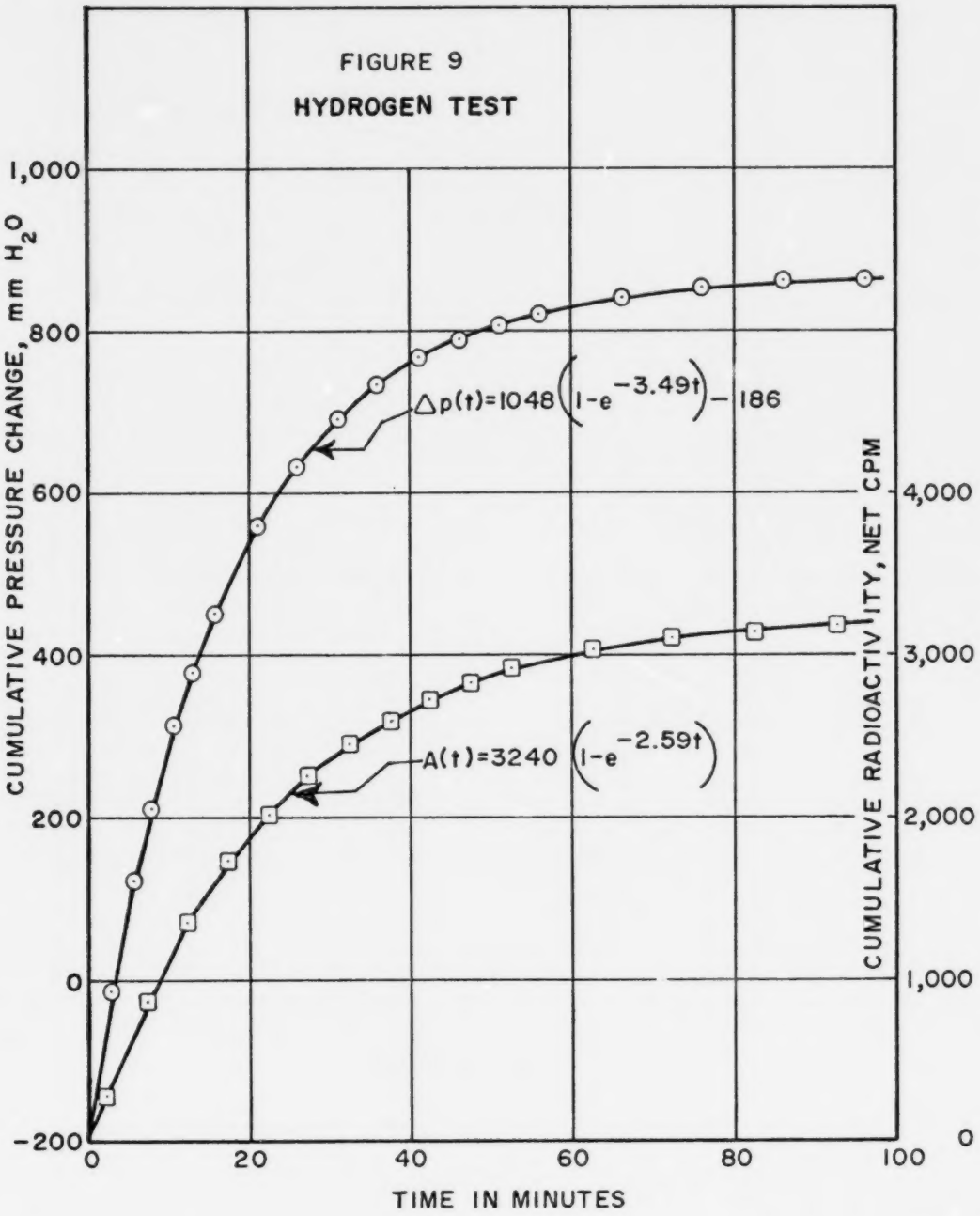


FIGURE 9
HYDROGEN TEST
CUMULATIVE PRESSURE CHANGE, mm H_2O
CUMULATIVE RADIOACTIVITY, NET CPM
TIME IN MINUTES
1,000
800
600
400
200
0
-200
4,000
3,000
2,000
1,000
0
0
20
40
60
80
100
$\Delta p(t)=1048\left(1-e^{-3.49t}\right)-186$
$A(t)=3240\left(1-e^{-2.59t}\right)$

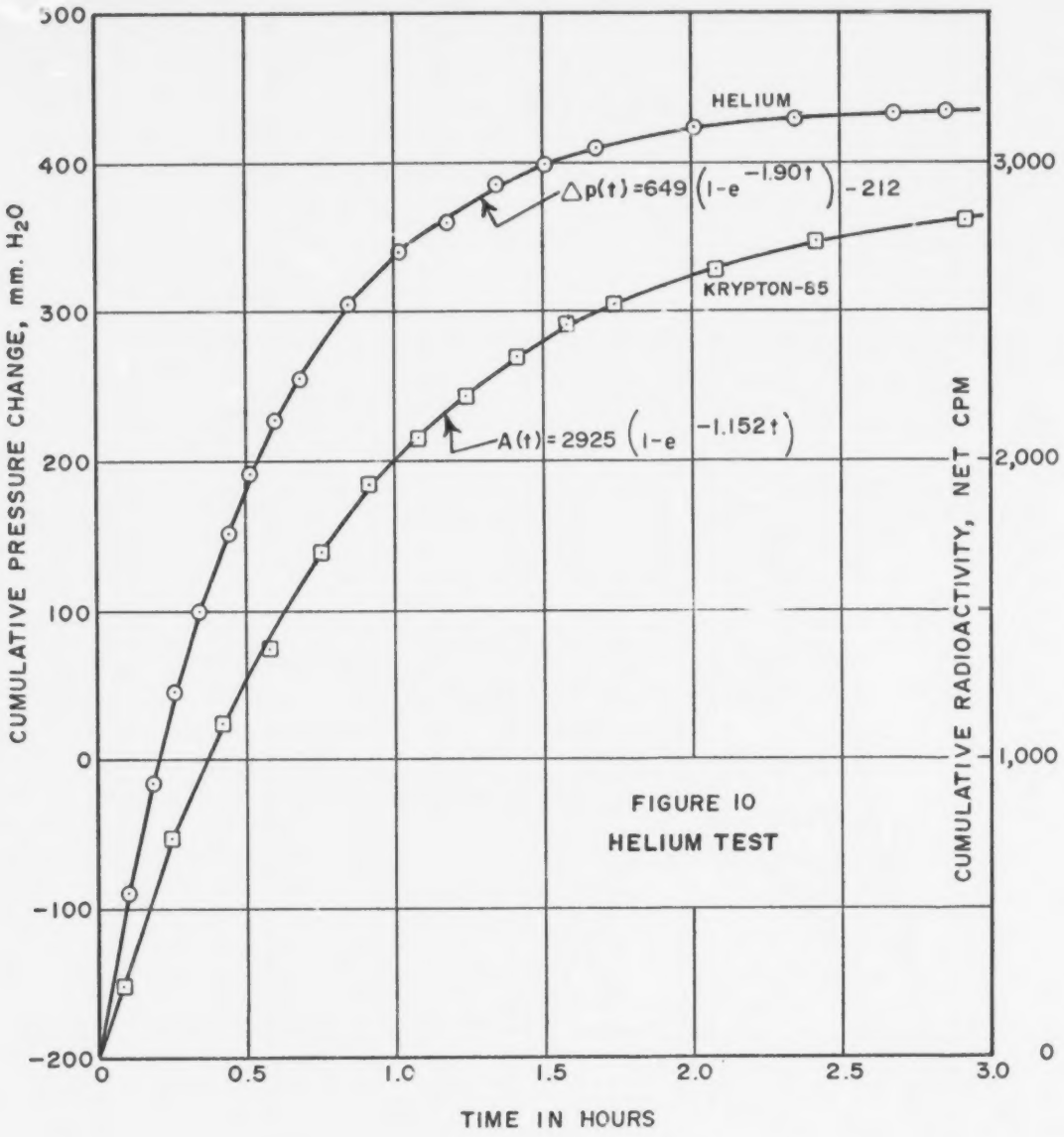


FIGURE 10
HELIUM TEST

TABLE III.—Helium-krypton-85 tests, 20° C.

K_z/hr			Solubility of helium		
Krypton-85	Helium	$(\frac{K_{Kr}}{K_{He}})$	$c_{gw}(\infty)$, mg/l	$c^{H}_{gw}(\infty)$,* mg/l	$\{\frac{c_{gw}(\infty)}{c^{H}_{gw}(\infty)}\}$
1.54	3.55	0.434	1.42	1.44	0.986
1.68	3.73	0.451	1.33	1.42	0.937
1.28	2.90	0.441	1.36	1.42	0.958
0.994	2.14	0.465	1.47	1.41	1.043
0.766	1.77	0.433	1.41	1.42	0.993
0.292	0.667	0.438	1.32	1.41	0.936
0.239	0.589	0.406	1.35	1.38	0.978

*$k_H = 10.9 \times 10^7$ mm/mole fraction.

TABLE IV.—Nitrogen-krypton-85 tests, 20° C.

K_z/hr			Solubility of nitrogen		
Krypton-85	Nitrogen	$(\frac{K_{Kr}}{K_{N_2}})$	$c_{gw}(\infty)$, mg/l	$c^{H}_{gw}(\infty)$,* mg/l	$\{\frac{c^{H}_{gw}(\infty)}{c^{H}_{gw}(\infty)}\}$
3.32	3.89	0.854	17.5	19.0	0.921
2.69	2.96	0.909	14.5	16.0	0.906
2.57	2.79	0.922	17.2	18.5	0.930
2.24	2.50	0.896	16.5	17.7	0.932
2.12	2.29	0.926	19.0	20.0	0.950
1.37	1.51	0.908	17.9	18.0	0.995
1.01	1.08	0.935	16.8	18.6	0.904
0.590	0.634	0.931	16.2	17.0	0.953
0.191	0.218	0.876	15.2	16.3	0.932

*$k_H = 5.93 \times 10^7$ mm/mole fraction.

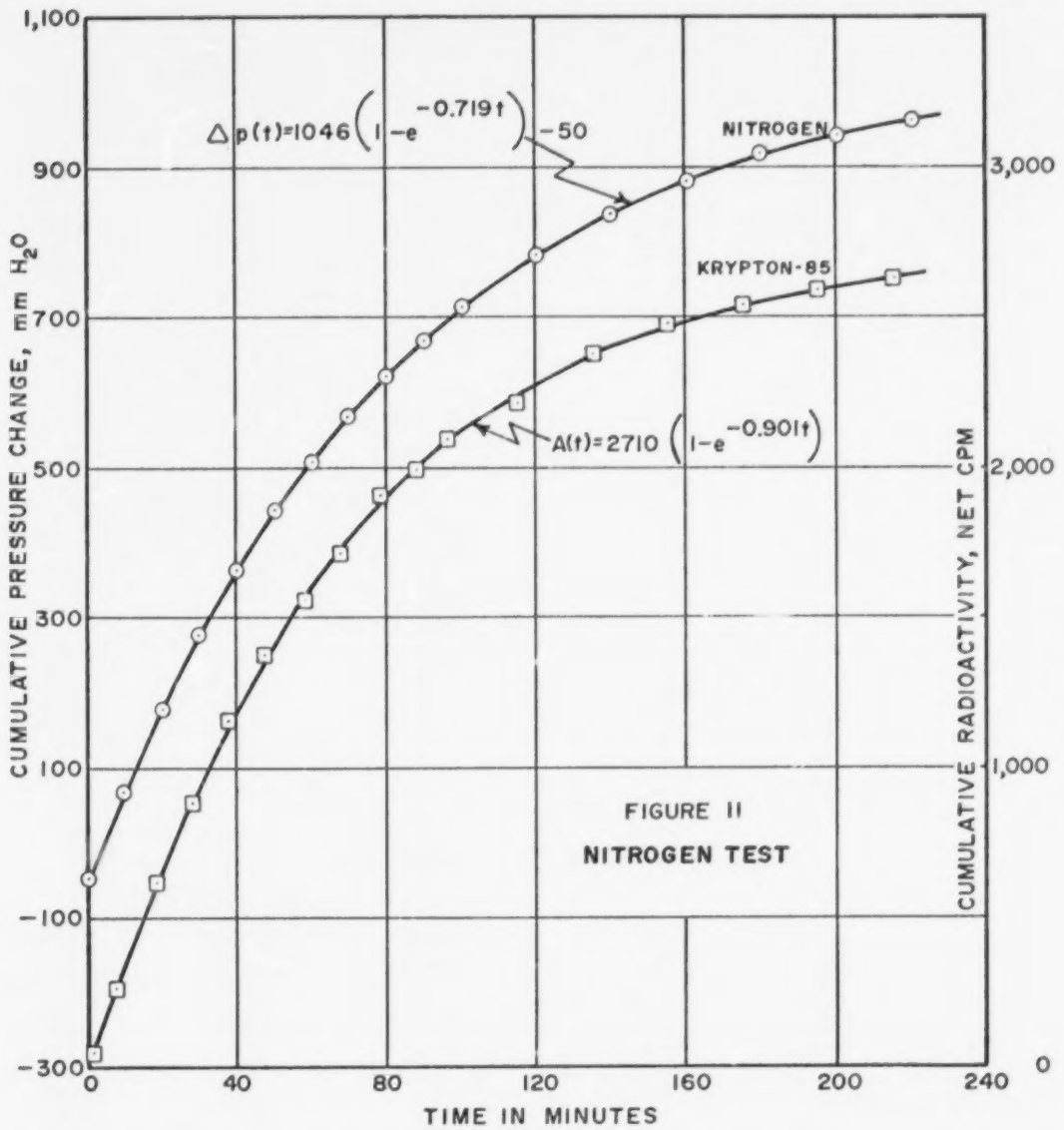
TABLE V.—Oxygen-krypton-85 tests, 20° C.

K_z/hr			Solubility of oxygen		
Krypton-85	Oxygen	$(\frac{K_{Kr}}{K_{O_2}})$	$c_{gw}(\infty)$, mg/l	$c^{H}_{gw}(\infty)$,* mg/l	$\{\frac{c_{gw}(\infty)}{c^{H}_{gw}(\infty)}\}$
2.56	2.86	0.895	36.1	36.7	0.983
2.25	2.84	0.792	35.5	36.5	0.973
2.17	2.45	0.885	35.8	36.7	0.97(
1.34	1.70	0.789	35.0	35.5	0.985
1.29	1.55	0.832	33.1	37.1	0.892
1.08	1.24	0.871	33.4	34.6	0.965
0.662	0.729	0.909	32.3	35.1	0.920
0.310	0.392	0.790	29.2	33.8	0.864
0.299	0.352	0.850	31.0	34.4	0.901
0.154	0.183	0.842	27.2	29.4	0.925

*$k_H = 3.04 \times 10^7$ mm/mole fraction.

Nitrogen-Krypton-85 Tests.—Table IV contains the results for the nine tests that were conducted using krypton-85 tracer gas in pure nitrogen, and Figure 11 shows typical reaction curves for the two gases.

The gas exchange ratios for the nitrogen-krypton-85 tests ranged from 0.854 to 0.935, averaged 0.906, and had a standard deviation of 0.027. The median gas transfer ratio was 0.909. On the average, the tests achieved 93.6 percent of the



Henry's Law solubility, the individual test results varying from 90.4 to 99.5 percent. The average apparent initial test water D.O. for these tests was 0.16 mg/1, and the final apparent D.O. averaged 0.15 mg/1.

Oxygen-Krypton-85 Tests.—Ten tests using the krypton-85 tracer gas in pure oxygen were conducted. Figures 5 through 8, presented earlier, are typical reaction curves for the oxygen-krypton-85 series. The results of these reactor tests are presented in Table V.

The observed gas transfer ratios for this test series ranged from 0.789 to 0.909; the average ratio was 0.846, and the standard deviation of the ratios was 0.045. The median ratio was 0.846. The individual oxygen transfer coefficients ranged from 0.183 to 2.86 per hour. The comparison of observed and calculated Henry's Law final concentrations indicated that, on the average, the tests achieved 93.8 percent of the Henry's Law solubility. The initial average D.O.'s in these tests were somewhat higher than in the other test series,

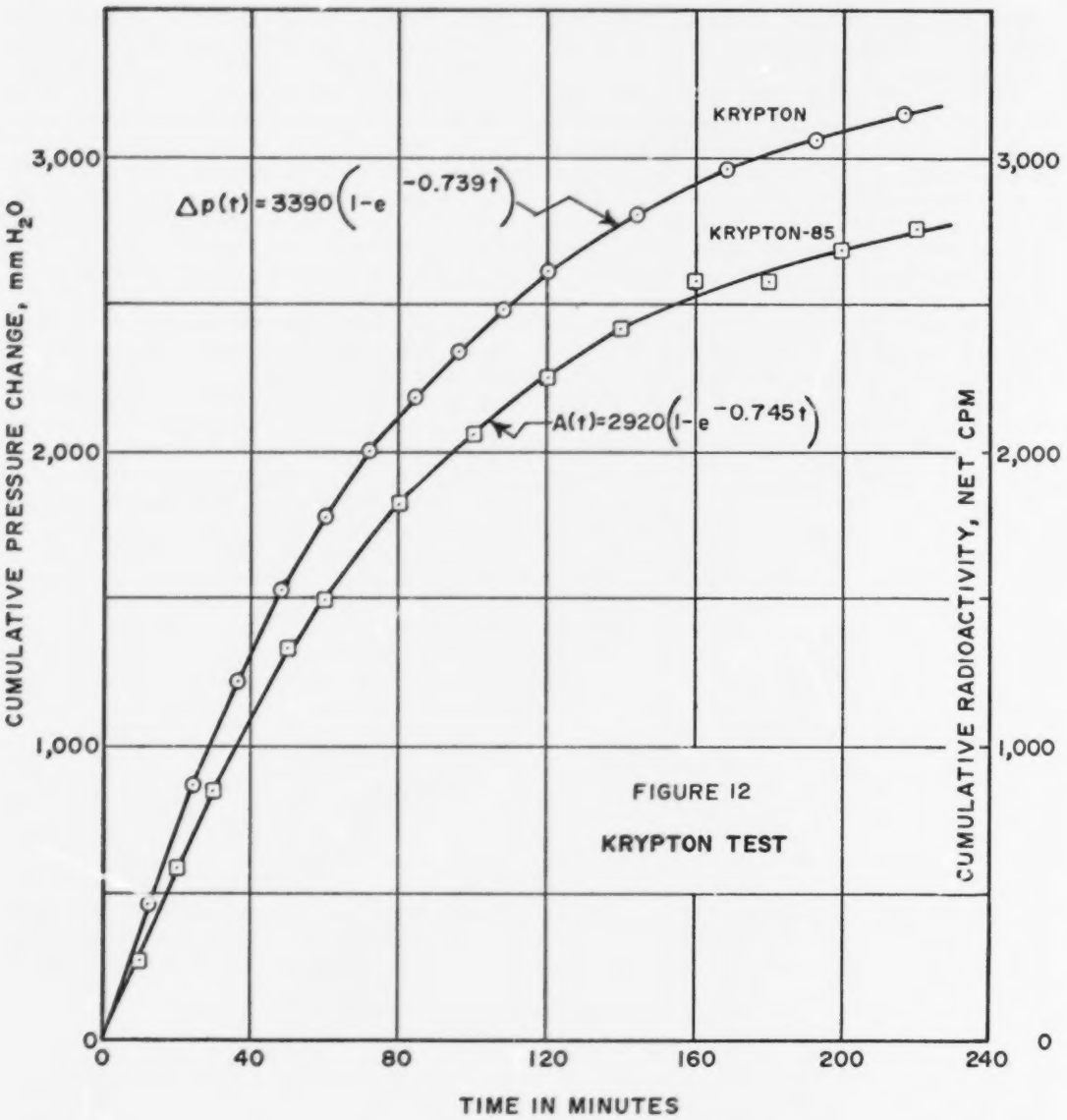


FIGURE 12

KRYPTON TEST

averaging 0.4 mg/1, and the significance of this result will be discussed in the section on sources of error. In the case of the oxygen tests, it was possible to make a final measurement of the dissolved gas concentration by means of the Winkler analytical method, and thereby to provide a check on the values calculated on the basis of the observed pressure changes. These results will also be discussed with the sources of error, rather than here, as they provide additional insight into the possible errors and their significance.

Three of the tests in the oxygen series (the first three tests in Table V) included a rough comparison of the effects of detergents on the gas exchange ratio. Specifically, all three tests were conducted with the same gas-to-liquid volume ratio (V_g/V_w); the first test listed in the table was performed with 0.5 mg/1 of ABS in solution, the second with 5.0 mg/1, and the third test shown contained no ABS. While these brief experiments are not definitive with regard to the effects of ABS, they do indicate that, although ABS may in-

crease the individual gas exchange coefficients somewhat, it had no apparent effect upon the gas exchange ratio.

As noted earlier, the open reactor tests first conducted with oxygen and krypton-85 produced an average gas exchange ratio of 0.82, compared to the average of 0.85 found in the closed constant volume reactor tests. Analysis of all of the results indicates that there is no statistically significant difference between these two average values, even though the two sets of tests were conducted in entirely different reactor systems. The earlier series in the open reactor was more extensive (26 separate tests). The average of all results from both test series leads to a final value of 0.83 for the ratio of K_2 values of krypton-85 and oxygen, respectively.

Krypton-Krypton-85 Tests.—As a final test series designed to verify the constant volume reactor experiment and to provide a positive measure of the range of expected error, if any, in the observed gas exchange ratios, a series of nine reactor tests was performed using trace quantities of krypton-85 in pure ordinary krypton, which is nonradioactive. Clearly, the gas exchange ratio for these tests should be 1.00, as the test is conducted with isotopes of the same gas. The results of these tests are tabulated below (Table VI), and a typical test is depicted in Figure 12.

The individual observed stable krypton gas exchange coefficients ranged from 0.172 to 2.09 per hour. The gas exchange ratio ranged from 0.938 to a high of 1.035, and averaged 0.990; the standard deviation of the ratios was 0.030. The median ratio was 0.993. On the average for these experiments, the final concentration of stable krypton in the test water was 93.5 percent of the Henry's Law concentration, with the individual results ranging from 91.0 to 96.7 percent. The apparent initial and final average Winkler D.O.'s of the test water were both 0.13 mg/1, indicating complete initial degassification of the test water and no air leaks into the system during the tests.

The observed average gas exchange ratio of 0.990 provides full general verification of the constant volume reactor test system and experiment, this value being insignificantly different from the expected value of 1.00. The tests again failed to achieve the full Henry's Law solubility, and in the same degree that has been noted before for the other test series. This will be discussed further below, but it should be noted here that the observed gas exchange ratio of 0.990 provides clear and independent evidence that the apparent discrepancy in regard to solubility has had no significant effect on the observed gas exchange ratios.

Figure 13 is a summary graph of all of the test results, and shows the individual test gas exchange coefficients versus the tracer gas K_2 in each case. The straight lines have been drawn through the origin and the average ratio for each gas, and the slopes of the lines are therefore the average gas transfer ratios. As may be seen, the observed data fit the individual straight lines very well for each gas, and deviations from the straight lines are random.

Figure 14 shows all of the individual krypton-85 transfer coefficients for all tests plotted against the gas-to-liquid volume ratios for the individual tests. These data provide a clear description of the mixing that occurred in the constant volume reactor and its effects on gas transfer. For the higher values of (V_g/V_w) the recirculated test water entered the reactor at or above the water surface, and the surface was broken; mixing under these conditions was apparently very good in

TABLE VI.—Krypton-krypton-85 tests, 20° C.

K_2/hr			Solubility of krypton		
Krypton-85	Krypton	$\left(\frac{K_{Kr\text{-}85}}{K_{Kr}}\right)$	$c_{gw}(\infty)$, mg/1	$c^{H}_{gw}(\infty)$,* mg/1	$\left\{\frac{c_{gw}(\infty)}{c^{H}_{gw}(\infty)}\right\}$
2.11	2.09	1.010	149	162	0.920
1.78	1.72	1.035	148	160	0.925
1.47	1.48	0.993	150	160	0.938
1.09	1.09	1.000	151	157	0.961
1.25	1.26	0.992	143	156	0.917
0.649	0.658	0.987	145	150	0.967
0.615	0.656	0.938	140	150	0.933
0.471	0.467	1.008	132	145	0.910
0.163	0.172	0.948	119	126	0.944

*$k_H = 1.52 \times 10^7$ mm/mole fraction.

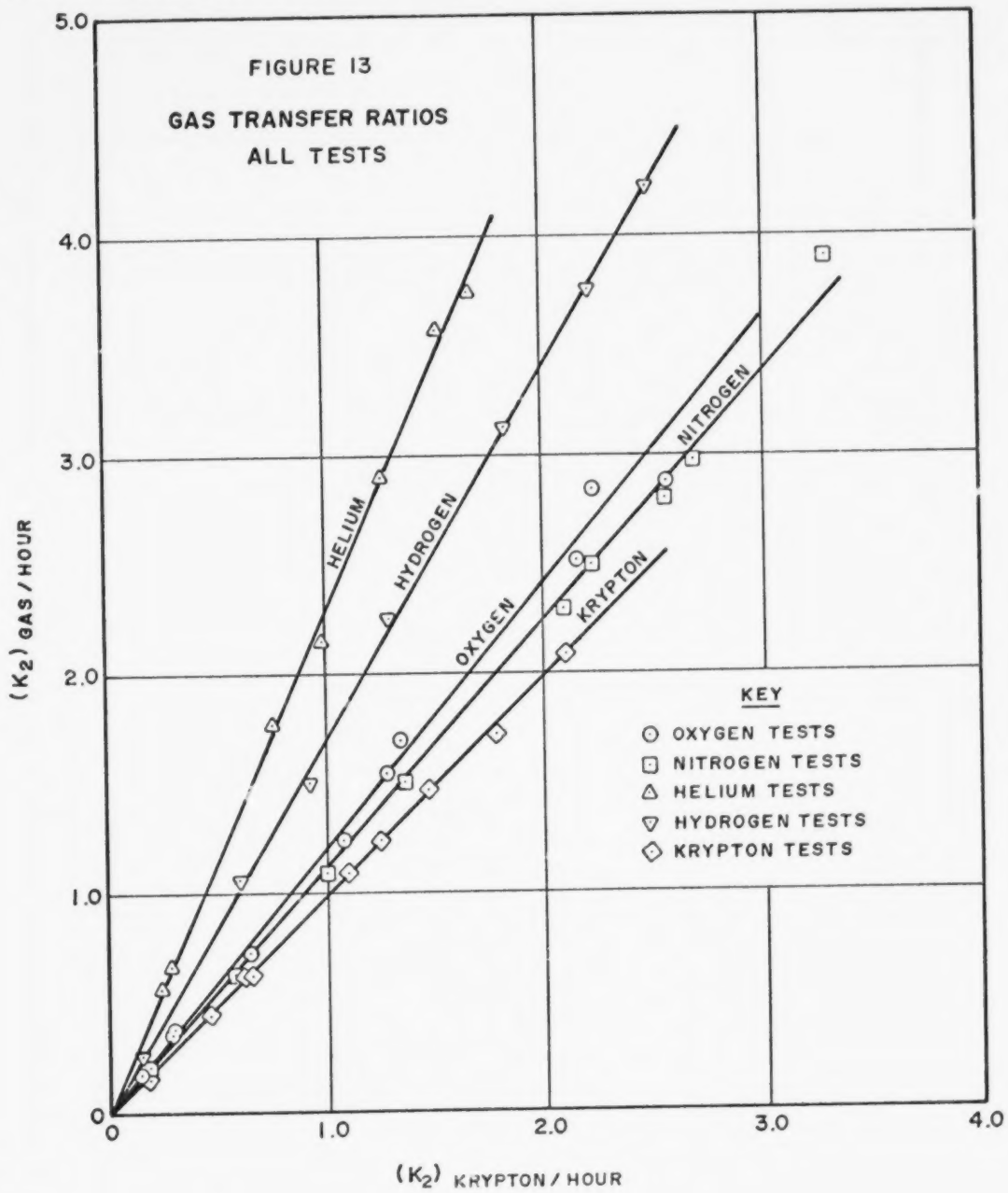


FIGURE 13
GAS TRANSFER RATIOS
ALL TESTS
5.0
4.0
3.0
2.0
1.0
0
0
1.0
2.0
3.0
4.0
(K2) GAS / HOUR
(K2) KRYPTON / HOUR
HELIUM
HYDROGEN
OXYGEN
NITROGEN
KRYPTON
KEY
OXYGEN TESTS
NITROGEN TESTS
HELIUM TESTS
HYDROGEN TESTS
KRYPTON TESTS

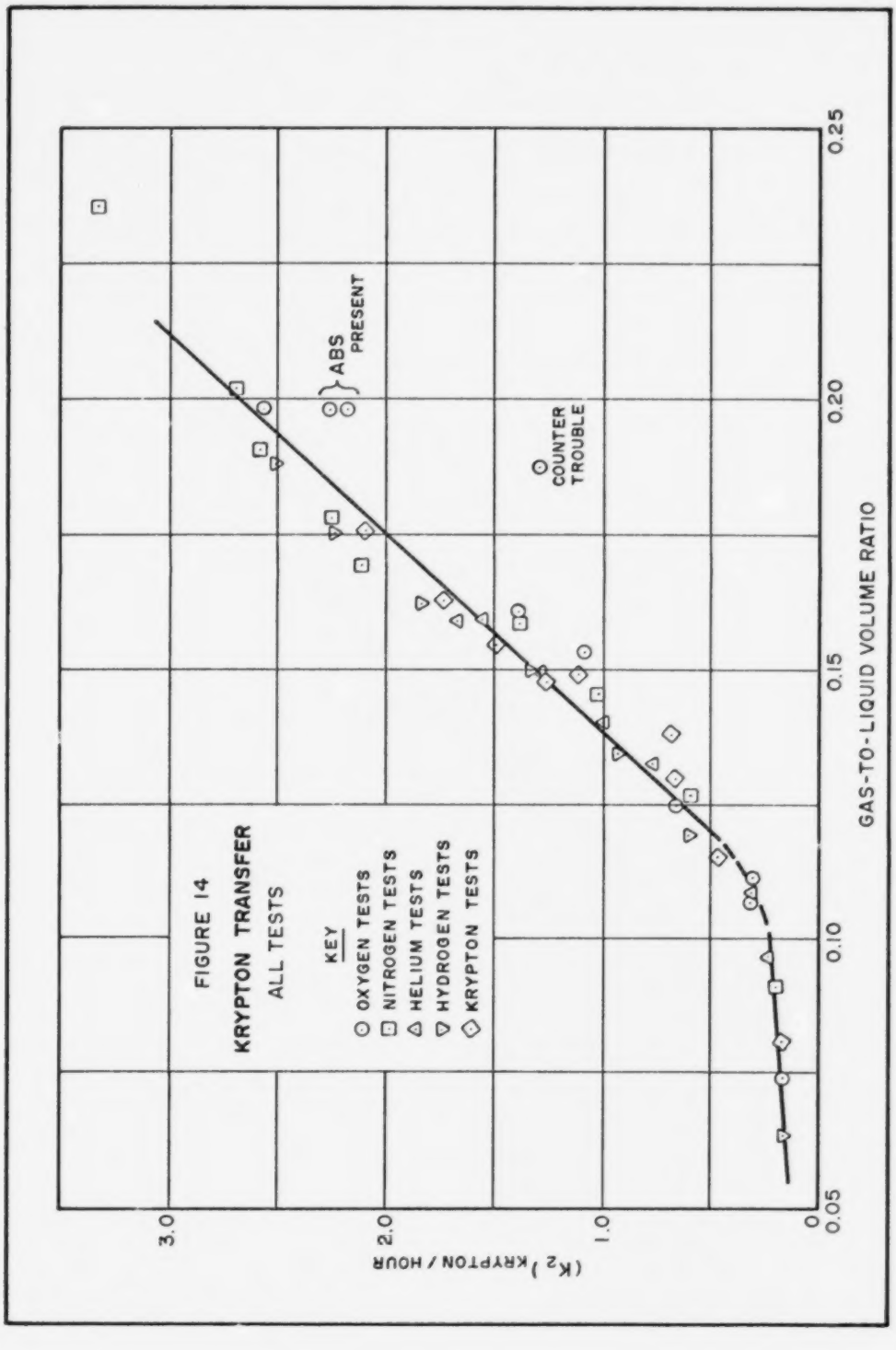


FIGURE 14
KRYPTON TRANSFER
ALL TESTS
KEY
OXYGEN TESTS
NITROGEN TESTS
HELIUM TESTS
HYDROGEN TESTS
KRYPTON TESTS
ABS PRESENT
COUNTER TROUBLE
$(K_2)_{KRYPTON}$ / HOUR
3.0
2.0
1.0
0
0.05
0.10
0.15
0.20
0.25
GAS-TO-LIQUID VOLUME RATIO

terms of replacement of the surface volume elements of water, as indicated by the steep slope of the straight line through the data. For values of (V_g/V_w) less than about 0.09 the recirculated water entered the reactor below the water surface, the surface was unbroken, and mixing was poor under these circumstances, in terms of renewal of the water surface layers. The slope of the line that fits these data is thus entirely different, and the water surface was apparently semilaminar. Mixing was therefore imperfect in the sense referred to in Chapter I. A transition from one type of surface mixing to the other occurred for values of (V_g/V_w) between about 0.09 and 0.12 or 0.13. Figure 14 also provides clear evidence of the general consistency of the gas exchange results for all of the tests in the constant volume reactor.

Other Gas Transfer Ratios.—The experimental results that have been presented also provide considerable information regarding the relative exchange capabilities of the several test gases, one to another, the tracer gas serving as the common factor. For instance, it is clear that the relative exchange capacities of hydrogen and nitrogen can be obtained from the hydrogen : krypton-85 and the nitrogen : krypton-85 ratios:

$$\frac{(\frac{K_{Kr}}{K_{N1}})}{(\frac{K_{Kr}}{K_{Hy}})} = (\frac{K_{Hy}}{K_{N1}}) = \frac{0.906}{0.586} = 1.54,$$

or, the ratio of K_2's of nitrogen to hydrogen, respectively, would be the inverse of the above, or 0.647. Similarly, the relative exchange capabilities of all of the pairs of gases that have been tested can be obtained readily, and it is therefore possible to compare the transfer capacities of all of the test gases.

Discussion and Summary, Constant Volume Reactor Tests

The open reactor and the constant volume reactor experiments that have been described provide highly useful information regarding the relative transfer capabilities of the various gases, and clearly demonstrate the usefulness of krypton-85 as a tracer for oxygen and other gases. The observed gas exchange ratios can be explained in terms of the molecular properties of the individual gases, and appear also to be related to the diffusivities of gases observed by others. Before proceeding to these interpretations, however, the sources of possible error in the observed ratios will be discussed.

Sources of Error.—Certain of the potential errors associated with the constant volume reactor experiment are of a random nature, or negligible, while others are not necessarily. Errors of a random type include the usual errors of measurement of observable quantities such as the volume of gas and the volume of water in any individual test and the changes of pressure and radioactivity with time, as well as the small errors that may be introduced in analysis of the test data. Errors of this type have been minimized in all possible ways, and would, in any event, be expected to average out to a negligible quantity in any series of tests. The standard deviations of the gas transfer ratios have been reported for each test series, and clearly indicate that such errors have been minimal and can be ignored. Errors of a consistent type that might affect the derived results are more difficult to discover and evaluate. However, the collective evidence provided by all of the experiments leads to clear conclusions regarding the consistent errors that might occur.

The observed data do indicate a consistent deviation from the expected gas transfer behavior in regard to the comparison between the observed and the Henry's Law solubilities of the several test gases. As has been noted, throughout the several test series the observed test gas solubility consistently averaged about 95 percent of the expected Henry's Law solubility. Although the extent of this discrepancy is quite small in terms of a possible effect on the observed gas exchange coefficients, the consistent nature of the discrepancy is of interest and requires explanation. Potential errors of a type that might lead to such a discrepancy have therefore been investigated. Such potential errors include the occurrence of gas leaks and the initial presence of gases in the test water, as well as the use of the ideal gas law for calculations.

Comparison of calculated results using van der Waals' equation in place of the ideal gas law demonstrates clearly that no significant error has been introduced through use of the ideal gas law, and that the differences between the results calculated by both methods are completely negligible for the conditions of these experiments. The observed krypton-to-krypton-85 average transfer ratio of 0.990 also indicates that such errors are negligible.

As regards the occurrence of gas leaks, the collective evidence shows clearly that these were

negligibly small or nonexistent for practical purposes. As has been noted, the experimental system was tested frequently, especially during the hydrogen and helium test series, for its ability to hold a positive pressure of these gases over long periods, usually overnight. In addition, the gas system was under a negative pressure during the individual tests, so that the presence of a gas leak would result in the entry of outside air. Any significant addition of outside air would result in an observable increase of the D.O. of the test water during the test. The triplicate Winkler D.O. determinations performed on the test water at the beginning and end of each experiment demonstrated that this did not occur in the hydrogen, helium, nitrogen and stable krypton test series, as the final average apparent D.O.'s were always the same or slightly less than the initial values. As has been noted, these apparent values were very low, in any case, and should be taken as real concentrations of zero for practical purposes. Finally, the tests with different isotopes of krypton, wherein the observed gas exchange ratio was exactly as expected, even though the observed solubility of stable krypton was not, also testify to the absence of significant gas leaks. Thus it has been concluded that significant gas leaks did not occur in the experiments to the extent that they would detectably affect the derived ratios or gas solubilities. (Conceivably, the two very light gases, hydrogen and/or helium, might be able to leak out of the reactor system through an opening that would not, however, permit the entry of significant quantities of air. In that event, however, either the observed reactions would not be simple first order or the gas pressure would approach a low, or zero, limiting value; the solubilities would then appear to exceed the Henry's Law solubility, and, since the system was tested nightly for leaks, the observed gas exchange ratios would not be as consistent as were found.)

The test water was initially rid of extraneous gases, principally oxygen and nitrogen, by boiling it for several hours under vacuum, a very effective procedure for these purposes. In addition, the procedure for transferring the test water into the reactor was carefully designed and performed to prevent any exposure of the test water to the atmosphere once it had been degassified, and no such exposure took place. The apparent initial and final D.O. of the test water of 0.1 or 0.2 mg/l most probably represented a real concentration of zero, and this conclusion is supported by the fact that there was no significant difference between the apparent initial and final D.O. concentrations in the tests with hydrogen, helium, nitrogen and nonradioactive krypton. The observed ratio of 0.990 for the krypton-krypton-85 tests also supports the conclusion that no significant quantities of extraneous gases were usually present, as does the agreement between the krypton-85 : oxygen transfer ratio of 0.82 for the open reactor tests and 0.85 for the closed reactor tests.

One further possibility remains, so far as explaining the observed discrepancy between the observed and Henry's Law solubilities of the test gases is concerned. This concerns the assumption made in the derivations and in the subsequent calculations that the initial concentration of test gas in the test water was zero. Both the experimental procedure and the observed results indicate that this assumption was not wholly correct, and that, in fact, a small amount of test gas probably did usually become dissolved in the test water before the experimental time zero was set and the observation and recording was begun. The extent to which this took place would definitely be reflected in the observed test gas solubility, but this type of error would not affect the observed gas exchange coefficients or ratios.

Recalling the experimental procedure, the reactor was initially filled completely with the degassified test water. A measured amount of water was then withdrawn, and the air that entered was removed by evacuating the space above the water. The test gas, containing a trace amount of krypton-85, was then introduced, the tracer gas supply tank put away, and necessary initial readings were made. Following this, the recirculating pump was switched on, time zero was thus fixed, and the measurement of radioactivity and pressure change was started. It is clear, therefore, that some initial exposure of the test gas and the test water did occur that was not reflected in the observed data. The duration of this exposure was minimized, but was of the order of two minutes. The possibility that test gas would dissolve in the water before the pump was started was recognized, but it was thought that the quantity of gas that would be involved was insignificant if the duration of exposure was minimized. Of course, the gas saturation deficit would be at its maximum at the same time, and the driving force for transfer therefore very great. The evidence presented below indicates that, even though the pump was off and the exposure was only 2 or 3 minutes, a significant amount of test gas did dissolve in the test water before the pump was

started and measurements begun. The quantity of gas involved is probably closely approximated by the amount of the discrepancy between the observed and the Henry's Law solubilities. This would in no way affect the shape of the observed gas transfer curves, or the observed gas exchange coefficients.

Two primary observations led to the above conclusion that $N_{gw}(O)$ was not zero in the constant volume reactor tests. The first, and most obvious, involves the test series with krypton-85 in ordinary pure krypton. In that series, even though an average of only 94 percent of the Henry's Law solubility was achieved, the gas exchange ratio was not affected to any observable degree, and did fully achieve the expected value. This clearly indicates an error of the type suspected, rather than one that would affect the exchange coefficients. The other evidence that $N_{gw}(O) \neq 0$ is provided by the series of tests using krypton-85 with pure oxygen, and is more direct. In that series an independent check on the course of the individual experiments was provided by Winkler D.O. analysis of triplicate test water samples taken on completion of each test. In one case (third from the bottom of table V), the average Winkler D.O. observed when the test was terminated actually exceeded by 1.0 mg/l the value of $c_{gw}(\infty)$ calculated on the basis of the observed reactor pressure changes. This was undoubtedly a test in which the duration of exposure of test gas and test water before starting the pump was longer than usual. It also was the test that involved the greatest discrepancy between the observed and the Henry's Law oxygen solubility. This provides the necessary clue to the principal source of the discrepancy.

For final verification, the infinite-time dissolved oxygen concentrations were calculated by two independent means: They were calculated as usual on the basis of the observed pressure changes in V_g, and these are the usual values of $c_{gw}(\infty)$ shown in table V; they were calculated also by projecting the observed average Winkler D.O. at the end of each test to the infinite-time concentration on the basis of the observed value of K_g. In six tests out of the total of 10, the value so calculated exceeded the value of $c_{gw}(\infty)$ by an amount ranging from 0.5 to 2.6 mg/l. In the other four cases, the value of $c_{gw}(\infty)$ exceeded the Winkler D.O.-based value by no more than 0.3 mg/l. The latter four cases are those showing the best agreement between $c_{gw}(\infty)$ and $c^{II}{}_{gw}(\infty)$ in table V. This provided positive evidence that the test gas itself was becoming dissolved in the test water to a significant degree before the experiment was started. It has therefore been concluded that this was the major source of the consistently observed 5 percent discrepancy between the values of $c_{gw}(\infty)$ and $c^{II}{}_{gw}(\infty)$ in the several test series. This type of experimental error has no effect whatsoever upon the observed gas exchange coefficients or their ratios.

As a result of the foregoing analysis of the potential and probable sources of error in the constant volume reactor tests, the average gas exchange ratios reported in the earlier section on experimental results are regarded as quite firm figures that contain no significant consistent error.

Summary, Constant Volume Reactor Tests.— Simultaneous gas transfer tests using hydrogen, helium, nitrogen, oxygen and ordinary krypton, each together with trace quantities of krypton-85, have been conducted in a constant volume gas exchange reactor. All tests were conducted at 20° C., and in all cases the direction of transfer of both the test gas and the tracer gas was into the test water from the overlying gas atmosphere. The individual gas transfer coefficients were varied by varying the kind of turbulent mixing that occurred in any test, particularly in regard to the replacement of the water surface layers, and usually varied within any test series by a factor of 10 or more. The ratio of the transfer coefficients of the test gas and the tracer gas was found to be a constant for each pair of gases, and was independent of the degree of mixing or the rate of surface replacement. In the test series using oxygen with krypton-85, the presence of detergent, in the form of ABS, in two of the tests, did not detectably affect the ratio of transfer coefficients. Analysis of the sources of error associated with these tests showed that for any test series the standard deviation of the observed gas transfer ratio was quite small, and ranged from 3 to 5 percent of the average ratio for the several gases tested. It was also shown that no consistent or systematic error was present in the observed ratios.

From these studies, the relative gas exchange capacities of any pair of the gases tested can be obtained. These results, taken together with the results from the earlier open reactor tests, can be interpreted in terms of the molecular properties of the gases, as will be shown in the following section of this report, and fully support the use of krypton-85 as a tracer for oxygen in turbulent water systems and in natural streams in particular.

mechanisms of gas transfer

CHAPTER THREE

INTRODUCTION

The available literature contains no clear and complete description of the underlying nature of the gas transfer or reaeration process. It is especially confusing in regard to the relative importance of molecular diffusion and turbulent mixing on gas transfer. This chapter therefore includes a detailed discussion of the reaeration process on the basis of what is currently known and what has been found in the experiments described earlier in this report. The basic reaeration model is developed from the simple considerations of the kinetics of gases, the relation between mixing and molecular diffusion is described, and these models are verified in terms of the available experimental evidence.

In an absolutely quiescent fluid medium, transfer of a dissolved gas downward through the depth is by molecular diffusion in accordance with Fick's law. If the gas concentration in the overlying atmosphere does not change with time, the rate of entry of gas molecules into the liquid is constant and relatively rapid, whereas the rate of escape to the atmosphere is proportional to the momentary concentration of dissolved gas molecules in the interfacial surface water layer (perhaps as much as several water molecules thick). The resistance of this thin interfacial water layer to entry of gas molecules from above is thought to be much smaller than the resistance of the deeper water layers to diffusion downward,[17,19] and in a quiescent fluid molecular diffusion of the dissolved gas molecules downward through the fluid is the slow and limiting process. Diffusion downward within the still fluid is described by Fick's law, which states that

$$J = -D_m \frac{dc}{dr} \qquad (31)$$

where J is the quantity of dissolved gas that diffuses per second across an area of 1 sq cm, D_m is the molecular diffusion coefficient for the specific gas in the specific medium, in cm^2/sec, and $\frac{dc}{dr}$ is the dissolved gas concentration gradient in the direction of transfer.

For the completely quiescent fluid, the concentration gradient at any depth is very small and hence the rate of diffusion downward is small. Dissolved gas molecules therefore accumulate in the interfacial surface water layer, and their concentration in this layer approaches the saturation concentration at a relatively early time. As a result,

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the net rate of gain of dissolved gas molecules (the rate of entry minus the rate of escape at the surface) soon becomes quite small, and gas transfer proceeds very slowly. The resulting slow overall rate of gas transfer is not due to a high surface resistance to entry, but rather is due to the blocking action of downward molecular diffusion within the fluid medium. It is diffusion within the fluid that limits the process in a quiescent fluid.

Mixing of the liquid layers greatly hastens the gas transfer process. It is at this point, namely the effects of mixing on gas transfer, that the literature becomes confusing. On the one hand, mixing of the fluid is regarded as affecting the rate of molecular diffusion, whereas in other views, gas transfer is thought to be directly accomplished by physical mixing, or "eddy diffusion." Throughout the literature it is commonly assumed that in a well-mixed fluid, mixing itself brings about a uniform concentration of the dissolved gas throughout the fluid depth, that thus there cannot be any concentration gradient within the fluid medium ($\frac{dc}{dr}=0$), and that the surface fluid layer must therefore always (and instantaneously) be saturated with dissolved gas. This view has required the further assumption of a laminar surface "film" of fluid that is not affected by mixing and across which there always exists a dissolved gas concentration gradient (saturation vs. gas concentration in the main body of fluid), otherwise it is thought that Fick's law could not apply and gas transfer could not take place at all.

These apparent conflicts between views, and between individual views and the real physical facts, can be resolved if we distinguish between what is known and what is speculative, and between what we observe and what must take place. Specifically, it is known by repeated observation that mixing does hasten gas transfer; it is also generally accepted that gas transfer must be in accordance with Fick's law; it is known by repeated observation that, at least under laboratory conditions, gas transfer takes place as a first order process in which the time rate of change of the saturation deficit is proportional to the deficit at any time, and this can also be shown on the basis of simple kinetic theory. It has also been observed repeatedly that in a well-mixed system there is no discernible variation of the dissolved gas concentration throughout the fluid depth. Other conditions being equal, it is known that a rise in temperature causes the rate of gas transfer to increase and the saturation concentration to decrease, and vice versa.

On the other hand, the existence of a laminar surface water film that is undisturbed by mixing, although it may be mathematically convenient, is purely speculative, as it cannot be directly or independently observed or demonstrated. The existence of such a film in a well-mixed fluid is intuitively very difficult to justify, and the film theory is not widely accepted in the physical sense. Nor can it be shown that the surface water layer, however thin, is either instantaneously or always saturated with dissolved gas in a turbulent system. Recalling that the process of solution at the surface must be a function of time, the assumption of a truly saturated surface water layer in a rapidly mixed system is difficult to defend. The observation that dissolved gas concentration is uniform or essentially so throughout liquid depth in a well-mixed system is undoubtedly valid, but the implied further conclusion that this is also true on the molecular scale is neither demonstrated nor probable. Specific mathematical models for the "rate of surface renewal," "frequency of mix," "film thickness," "age distribution of surface volume elements," and other similar conceptual but non-observable parameters, are speculations, not facts. Although such models may be convenient, and although it may be shown that they do not conflict with what can be observed, this does not constitute the necessary and sufficient proof that the models are, in fact, true representations of the real processes that take place.

The above conflicts may be resolved, and the nature of the gas transfer process in a turbulent water system clarified, by careful definition of terms and by making a clear distinction between the molecular and the macroscopic frames of reference. In the first place, it is necessary to distinguish carefully between the transfer of the dissolved gas molecules and the physical transport of the fluid volume elements. The fluid volume elements are transported from one location to another by physical mixing, or "eddy diffusion," and it is possible that for practical purposes mixing may bring about a homogeneous and uniform mixture of the volume elements of liquid. However, as so clearly described by Phelps,[10] mixing alone cannot result in a uniform *molecular* concentration of the dissolved gas:

"When it is realized that the surface film of contact is infinitely thin, it will be seen how impotent any degree of agitation must be. The final result of surface solution, plus mixing, is merely an intimate admixture of very thin layers of saturated water and relatively much thicker layers of unsaturated water, a sort of emulsion like oil in water which, no matter how highly emulsified, never

becomes a homogenous system. These facts are well expressed by Prof. G. H. Bryan;[1] 'To state the matter precisely, however finely two fluids have been subdivided by agitation, the molecular constitution of the different portions remains unchanged. The ultimate process by which the individual molecules of two different substances become mixed, producing finally a homogeneous mixture, is, in every case, diffusion.' "

Thus it appears clear that, although physical mixing and dispersion may result in a homogeneous mixture of the volume elements of the liquid, a truly uniform and homogeneous concentration of dissolved gas molecules can only be accomplished by molecular diffusion in accordance with Fick's law.

It is necessary to recognize also that we are unable to observe the gas transfer process on a molecular scale, and that what has been observed may therefore be deceptive. As has been noted earlier, a sample of water, no matter how small, contains a very large number of volume elements of water. The amount of dissolved gas in such a sample is measured only in terms of the total quantity of gas molecules, and this implies nothing at all about the *distribution* of dissolved gas molecules among the individual volume elements of water or within them. What is actually measured is the total quantity of gas in the sample, and from this the *average* concentration in the whole sample is deduced. It is entirely reasonable to suppose that the actual distribution of dissolved gas molecules is not uniform within the fluid volume elements or from one volume element to the next within the sample, and, in fact, this must be the case if Fick's law is to be applicable. Thus, in a well-mixed system we observe what appears to be the same average dissolved gas concentration at different locations, yet at the same time a dissolved gas concentration gradient exists between individual volume elements everywhere within the fluid. The concentration of dissolved gas is uniform only in terms of our ability to measure it, and not on a molecular basis.

One of our principal difficulties thus far in explaining the effects of mixing on gas transfer has been just this observation of an apparently uniform dissolved gas concentration throughout the main body of fluid in a well-mixed system. This has led to the erroneous argument that a concentration gradient cannot exist within the main body of fluid, and this, in turn, has required that we postulate a fictitious surface film across which a concentration gradient could exist. Indeed, review of the available literature on reaeration reveals that the very definition of "homogeneous mixing" has customarily been in terms of uniformity of the observable dissolved oxygen concentration—if there is no definitely observable difference between dissolved gas concentrations at different points within the fluid, the fluid has been said to be homogeneously stirred or mixed. When it is realized that we actually observe only the average gas molecule concentration in any sample, there is nothing inconsistent in the idea of a system in which the fluid volume elements are uniformly mixed but in which there is also a dissolved gas concentration gradient everywhere between neighboring fluid volume elements.

Thus, although transfer can only originate at the surface because the overlying atmosphere is the only source of additional dissolved gas molecules, *at any moment molecular diffusion takes place in all directions and everywhere in the whole volume of fluid.* In Fick's law, then, $\frac{dc}{dr}$ represents the *average* concentration gradient between neighboring volume elements of water everywhere in V, just as c represents the *average* dissolved gas concentration everywhere in V.

Scales of Reference

The following descriptions of gas transfer and reaeration in turbulent water require that clear distinctions be made among the several scales of reference that must be used. To recapitulate, these scales of reference range all the way from molecules at the one end to the whole volume of fluid at the other. The terms that relate them are defined and described as follows.

The *molecular scale* is of the order of angstrom units (10^{-8} cm.), and this is the size range of the dissolved gas molecules. A very large number of dissolved gas molecules (infinitely large for mathematical purposes) is contained in a *volume element* of fluid; the volume element is still an infinitesimal in the calculus sense. *Diffusion* refers to the movement of molecules of dissolved gas, whereas *mixing*, or dispersion, refers to the movement or transport of volume elements of fluid. (It may be recalled also that diffusion takes place due to the inherent kinetic energy of the gas molecules, whereas dispersion results from external forces being applied to the fluid).

A *sample*, no matter how small, contains a very large number of volume elements of fluid; it represents the smallest *observable* size range. A sample is thought of as representative of a *region* of fluid, and a region contains a relatively large number of samples. The *whole volume* of fluid may contain one or more regions, depending upon

whether mixing is uniform throughout the whole volume, or not.

THE REAERATION PROCESS

The Basic Reaeration Equation

Consider the interfacial surface layer of water in a gas-water system. This layer, no more than a few water molecules thick, consists of an infinitely large number of volume elements of water. The concentration of gas molecules in the overlying atmosphere is constant, and the gas does not react chemically with water. The entire volume of water is homogeneously mixed, in the specific sense that: (*a*) The rate of circulation and replacement of volume elements of water is the same everywhere in V, including the surface; (*b*) there is uniform *average* concentration of dissolved gas molecules everywhere in V; (*c*) there is uniform *average* dissolved gas concentration gradient everywhere in V; (*d*) there are no distinct hydrodynamic regions or films in V; (*e*) there is no *net* dissolved gas concentration gradient in any preferred direction within V.

The surface water layer in the homogeneously mixed fluid thus exists only in a statistical sense, as its individual volume elements are continually being replaced by others from below, by mixing. The average concentration of dissolved gas molecules in the surface water layer at any instant is the same as that in the main body of fluid. In the statistical sense, at any instant the surface water layer may be regarded as just having been replaced from below.

The momentary rate of change of the concentration of dissolved gas molecules in the surface layer is thus the result of the rate of entry from the overlying atmosphere, the rate of escape of once-dissolved gas molecules back into the atmosphere, the rate of molecular diffusion downward into the next deeper water layer, and the rate of molecular diffusion upward into the surface layer from the next deeper layer. By the definition of homogeneous mixing, the average concentration of dissolved gas molecules is the same everywhere in V; molecular diffusion of dissolved gas molecules between neighboring volume elements of water is the same in all directions and at all locations within V. Hence, the average concentration of dissolved gas molecules in the just-replaced surface water layer is the same as that in the next deeper water layer, and the rate of molecular diffusion downward from the surface layer is the same as the rate of diffusion upward from the next deeper layer. The net rate of molecular diffusion across the boundary between the surface layer and the next deeper water layer is therefore zero. The net rate of change of the concentration of dissolved gas molecules in the interfacial surface water layer is therefore just the rate of entry from the overlying atmosphere minus the rate of escape to the atmosphere from the interfacial surface water layer.

The thickness of the interfacial surface water layer thus represents that thickness of water from which dissolved gas molecules can escape directly to the atmosphere, or the thickness through which they must diffuse to reach the atmosphere. Although this thickness may differ for water systems that contain different concentrations and kinds of polluting materials, it will not change during the course of any one experiment. Also it will be the same thickness for clean water in any system, at constant temperature.

(In an absolutely quiescent fluid, in contrast to the above, there is no intermixing of volume elements of water or of water layers, and a positive net rate of molecular diffusion of dissolved gas molecules downward within V occurs. Of course, a truly quiescent fluid is virtually impossible to achieve experimentally, so this distinction is conceptual rather than actual.)

Let r_e be the rate of entry of gas molecules into the interfacial surface water layer from above, expressed as mg/unit time. The rate of entry is proportional to C_g, the concentration of gas molecules in the overlying atmosphere, and, since C_g is constant, the rate of entry is also constant throughout the course of any experiment at constant temperature.

The rate of escape of gas molecules from the interfacial surface water layer is proportional to C_w, the concentration of dissolved gas molecules in this layer. Let h be the thickness of the surface water layer from which dissolved gas molecules can escape directly to the overlying atmosphere. The thickness h is analogous to the mean free path of the gas molecules in the water medium, but may not be the same because of the movement across the interfacial surface. Thus, h is also the volume of water/cm^2 of surface that contains all of the dissolved gas molecules that are available at any moment for escape. The product (hC_w) is therefore the number of gas molecules available for escape, expressed as mg/cm^2 of surface.

If n is the number of new surface layers of thickness h that are exposed per unit time and A is the surface area in cm^2, then the product (nA)

is the rate of exposure of new surface area in cm^2/unit time. The product (hC_wnA) is then the total number of dissolved gas molecules that become available for escape, expressed as mg/unit time. Only a small fraction of these available molecules actually move in the necessary direction and possess the necessary energy to cross the interface and escape; at any moment, the actual rate of escape, r_o, expressed as mg/unit time, is proportional to the number of molecules available for escape, and, letting b represent the necessary dimensionless proportionality constant,

$$r_o = b(hC_wnA)$$

The net rate of gain of dissolved gas molecules in the interfacial surface water layer (and therefore in all of V) is just the rate of entry minus the rate of escape, or

$$(r_e - r_o) = r_e - b(hC_wnA)$$

By definition, the water is saturated with dissolved gas molecules when the rate of entry from the overlying atmosphere is just equal to the rate of escape from the interfacial surface water layer. Under these circumstances $(r_e - r_o) = 0$, and it is found that

$$r_e = b(hC_snA),$$

where C_s is the saturation concentration of dissolved gas molecules in the water. Hence,

$$(r_e - r_o) = bh(C_s - C_w)nA$$

If we divide both sides of the above equation by V, the whole volume of water in liters, we then have the net rate of gain of dissolved gas molecules, expressed as mg/liter per unit time. But this is also just the rate of change of concentration, $\frac{dC}{dt}$, for the surface water layer, and, by the definition of homogeneous mixing, also for the whole volume, V. It thus follows that

$$\frac{dC}{dt} = \frac{bhnA}{V}(C_s - C)$$

where C is the average dissolved gas concentration in V. In the homogeneously mixed system, $(C_s - C) = D$, the saturation deficit, and

$$\frac{dC}{dt} = \frac{d}{dt}(C_s - D) = -\frac{dD}{dt}$$

whence

$$\frac{dD}{dt} = -\frac{bhnA}{V}D \qquad (32)$$

Letting $(\frac{bhnA}{V}) = K_2$ we now obtain the familiar first order reaction model for gas transfer in a homogeneously mixed water system, namely

$$\frac{dD}{dt} = -K_2D \qquad (33)$$

It is clear from this development of the basic reaeration equation that the volumetric reaction rate coefficient, K_2, is directly dependent upon the surface area of contact, the rate at which the surface is replaced by other volume elements of water, and the ability of the dissolved gas molecules to escape across the interface, and is inversely proportional to the volume of water. For the same V, the larger the surface area of contact (or the smaller the depth) the larger the value of K_2. If both A and V are kept the same, then the numerical value of K_2 is directly and wholly dependent upon the rate of surface replacement at any temperature, the quality of water being unchanged. Thus K_2, the observable bulk gas transfer coefficient, is most suitably regarded as a measure of the actual degree of mixing, in terms of surface replacement, other conditions being equal.

It should be noted that the quotient $(\frac{V}{A})$ is the actual whole depth of water *only* under conditions of homogeneous mixing. Also, the process by which a dissolved gas molecule crosses the interface to become free is not molecular diffusion in the usual sense. Diffusion coefficients, as represented by Fick's law, reflect the diffusion of molecules within a single medium, rather than their passage from one medium to another. Although the two processes are by nature the same, the coefficient b (or bh) reflects the ability of the gas molecule to cross an interface, whereas the Fickian coefficient D_m reflects its ability only to diffuse within the water medium.

It is clear also from the foregoing that for any specific system in which h, A and V are fixed (for example, a stirred beaker of water), the **maximum** value of K_2 is attained when mixing is homogeneous. If mixing is not homogeneous, then the dimensionless surface volume replacement ratio $(\frac{nhA}{V})$ will be reduced and K_2 will be lower.

Effect of Temperature and Contaminants

Any change in the quality of the water or in the kinetic energy of the dissolved gas molecules will cause a corresponding change in the ability of the dissolved gas molecules to escape. The changed rate of escape can be viewed either as the result of

a change in h (the thickness of interfacial surface water layer from which dissolved gas molecules can escape) or as the result of a change in b (the fraction of available dissolved gas molecules that escapes from the same thickness of surface water layer). Regardless of which view is preferred, the net result is a change in the rate of escape of dissolved gas molecules and an associated change in K_2, other conditions being equal.

Effect of Contaminants.—The presence of a contaminant such as an oil or a detergent changes the character of the interfacial surface water layer, and thus causes a change in the ability of the gas molecules to penetrate the surface and escape. This may be due to the physical interspersing of molecules other than water, or by the actual superposition of an additional layer of the contaminant. In either case, the value of b (or h) will be modified accordingly, and so will the observed K_2.

Effect of Temperature.—A change of water temperature is associated with a corresponding change in the inherent kinetic energy of the dissolved gas molecules, and this modifies their ability to escape from the interfacial surface water layer. Thus, for instance, a rise in water temperature also means that the dissolved gas molecules possess additional kinetic energy, and this will be associated with a higher value of b or h. For the same A, V and n, this must result in an increased value of K_2, as is observed experimentally.

Recalling that the net rate of gain of dissolved gas molecules per unit time is zero when the water is saturated with dissolved gas, and that under these circumstances the constant $r_e = bhC_s nA$, it also follows that an increase in the value of b or h due to a rise in water temperature must be associated with a corresponding decrease in the value of C_s, and vice versa. Thus a change in water temperature also results in a change in the value of the dissolved gas saturation concentration in the direction that is observed experimentally.

The foregoing development now permits numerical evaluation of the effect of temperature on the observable value of K_2. If the temperature of the overlying atmosphere remains unchanged, and if a change in water temperature causes a corresponding change in b (the fraction of available molecules that escapes from the same h), then reference to the definition of saturation indicates that

$$r_e = b(T_1)hnAC_s(T_1) = b(T_2)hnAC_s(T_2)$$

where T_1 and T_2 are two different water temperatures. (The rate of entry, r_e, is proportional to C_g, and C_g and r_e are constant here, since only the water temperature has been changed.) Therefore,

$$b(T_2) = b(T_1)\frac{C_s(T_1)}{C_s(T_2)}$$

Also, recalling that $K_2 = \left(\frac{bhnA}{V}\right)$,

$$\frac{K_2(T_2)}{K_2(T_1)} = \frac{b(T_2)}{b(T_1)}$$

Substitution for $b(T_2)$ in the last equation yields

$$\frac{K_2(T_2)}{K_2(T_1)} = \frac{C_s(T_1)}{C_s(T_2)}$$

The above equation now permits a direct evaluation of the effect of changes in water temperature upon the transfer coefficient, K_2, in terms of the known values of the saturation concentrations of dissolved oxygen in water from the more exact van't Hoff-Arrhenius equation, the usual expression that is taken to describe the effect of water temperature on K_2 is

$$\frac{K_2(T_2)}{K_2(T_1)} = \theta^{(T_2 - T_1)}$$

where θ is the temperature coefficient. (For practical purposes here the coefficient, θ, may be treated as a constant over the temperature range of interest, even though it is not a true constant over a wider range.) Hence we wish to evaluate the coefficient θ by use of the expression

$$\frac{K_2(T_2)}{K_2(T_1)} = \theta^{(T_2 - T_1)} = \frac{C_s(T_1)}{C_s(T_2)} \qquad (34)$$

and on the basis of the available numerical values of the dissolved oxygen saturation concentrations at various temperatures. Using the known dissolved oxygen saturation concentrations in clean water and at standard atmospheric pressure for temperatures from 0° C. to 30° C.,[16] it is found that the resulting calculated values of θ lie within the range

$$1.018 \leq \theta \leq 1.026$$

The mean value is $\theta = 1.022$, and for the entire range of calculated results,

$$\theta_{mean} = 1.022 \pm 0.004$$

in the temperature range 0° C. to 30° C. Thus, all of the calculated values of θ lie within 0.4 percent of the mean value in this temperature range.

The available dissolved oxygen saturation limits

for water containing large quantities of dissolved salts provide further verification of the numerical value of the temperature coefficient, θ. Specifically, using in equation (34) the known dissolved oxygen saturation limits for sea water containing 20,000 mg/l of chloride at standard pressure,[16] the resulting calculated values of θ all lie between the limits 1.019 and 1.025. The mean value is 1.022, as found for clean water, and for the temperature range 0° C. to 30° C. we obtain for sea water

$$\theta_{mean} = 1.022 \pm 0.003$$

Thus, the presence of dissolved chlorides in sea water has no significant effect upon the temperature coefficient, θ, that is used to correct observed or estimated values of K_2 from one temperature to another in the usual range of interest.

In regard to the above results, it should first be noted that the available numerical values of C_s at various temperatures may not safely be presumed to be accurate within such narrow limits ($\pm 0.4\%$). Also, our ability to observe the relation between K_2 and temperature in the laboratory involves a considerably greater degree of experimental error. Thus, the calculated range for θ of 1.018 to 1.026 may or may not be real. At least for the present, the mean value for θ of 1.022 appears to be entirely satisfactory for practical purposes within the range 0° C. to 30° C., but should not be extrapolated much beyond this range.

The predicted mean value of $\theta = 1.022$ agrees excellently with the value of 1.024 observed experimentally by Churchill et al. in their extensive studies,[13] and this is taken to be the best of experimental verification of the predicted result and of the foregoing developments.

Relation Between K_2 and Diffusivity

In a homogeneously mixed fluid, both mixing and molecular diffusion take place simultaneously. Mixing of the fluid volume elements hastens the bulk gas transfer process across the water surface to the extent indicated by equation (32), but transfer of the dissolved gas molecules within the whole volume V must take place by molecular diffusion according to Fick's Law, equation (31). Transfer of the gas can only originate at the water surface, because the only source of additional gas is located above the surface. Hence, the bulk gas transfer process at the surface and the molecular diffusion process within V both reflect the net rate of gain of dissolved gas molecules at the surface, and, in essence, diffusion within V keeps pace with bulk transfer at the surface. Thus, equations (31) and (32) must apply simultaneously. Rearranging the terms of equations (32) and (33) and converting to the same units, and combining with equation (31) yields

$$J = -D_m \frac{dc}{dr} = \frac{V}{A}\frac{dD}{dt} = -(bhn)D = -KD\frac{V}{A} \quad (35)$$

where J is the net quantity of gas transferred into the water in mg/cm²/sec, D is the average saturation deficit in mg/liter, V is the whole volume in liters, A is the area of contact in cm², and K now represents the volumetric gas transfer coefficient, K_2, with units/sec. D_m is the usual molecular diffusion coefficient that reflects the ability of the dissolved gas molecules to diffuse from one volume element of water to another within the main body of fluid, and $\frac{dc}{dr}$ is the mean dissolved gas concentration gradient between neighboring volume elements of water everywhere in V. As noted earlier, this concentration gradient is multidirectional, and gas transfer by diffusion within V has no preferred direction in the homogeneously mixed system.

If we now consider the simultaneous transfer of two gases in a uniformly mixed system where the water was initially completely degassified and where the gas concentrations in the overlying atmosphere do not change with time, it follows from equation (35) that

$$\frac{K_1}{K_2} = \frac{(D_m)_1\ (\frac{1}{D_1})(\frac{dc_1}{dr})}{(D_m)_2\ (\frac{1}{D_2})(\frac{dc_2}{dr})} \quad (36)$$

where the numerical subscripts now identify the two gases. But for the two specific gases transferring simultaneously

$$\frac{K_1}{K_2} = \text{constant} = a_1$$

and

$$\frac{(D_m)_1}{(D_m)_2} = \text{constant} = a_2$$

whence

$$\frac{(\frac{1}{D_1})(\frac{dc_1}{dr})}{(\frac{1}{D_2})(\frac{dc_2}{dr})} = \frac{a_1}{a_2} = \text{constant} = a_3$$

and therefore

$$\frac{K_1}{K_2} = (\text{constant})\frac{(D_m)_1}{(D_m)_2} = a_3\frac{(D_m)_1}{(D_m)_2} \quad (37)$$

Analytical evaluation of the constant a_3 is difficult, because there is no way of knowing the mean concentration gradient for all of V at any instant. However, it seems intuitively that the escape coefficient b referred to earlier (the fraction of available dissolved gas molecules that actually escapes) should be proportional to the diffusivity for any gas. For two substances diffusing simultaneously in the same medium, Einstein's law of diffusion indicates that the only difference between their diffusion coefficients results from the difference with which the medium resists the passage of the two different kinds of molecules, i.e., from the two different friction coefficients. Since the medium is identical for diffusion of both substances, the relative diffusivity of the two substances is a function only of the difference in the physical properties of the substances themselves. Therefore, although the resistance of the interfacial water surface may be numerically different from the frictional resistance to diffusion within the medium, so far as the escape of two gases is concerned, the relative resistance of the surface to escape and the relative frictional resistance to diffusion within the medium should not be different. For the two gases transferring simultaneously in water, the surface barrier presented to both is identical, and it therefore appears that the following relation should be applicable:

$$\frac{(D_m)_1}{(D_m)_2} = \frac{b_1}{b_2}$$

If this is so, then it follows from the expression $K = \frac{bhnA}{V}$ that $a_1 = a_2$, and hence that $a_3 = 1$.

From a different view entirely, consider the momentary molecular diffusion process between two immediately adjacent volume elements of water at the instant they come together, at some time after the start of the experiment. The maximum possible saturation deficit in one of the volume elements is just C_s (if, for instance, this volume element has never been exposed to others that contain dissolved gas and has never visited the surface), and the maximum possible dissolved gas concentration in the other volume element is C_s (suppose this one was at the surface an instant ago and had previously been at the surface for a long time). For this special case

$$\frac{(\frac{1}{D_1})(\frac{dc_1}{dr})}{(\frac{1}{D_2})(\frac{dc_2}{dr})} \simeq \frac{\frac{1}{(C_s)_1} \times \frac{(C_s)_1}{(\Delta r)}}{\frac{1}{(C_s)_2} \times \frac{(C_s)_2}{(\Delta r)}} = 1$$

Thus, conceptually, the constant a_3 has the value unity for an experiment involving the simultaneous transfer of two gases, and this leads to the result

$$\frac{K_1}{K_2} = \frac{(D_m)_1}{(D_m)_2} \quad (38)$$

At a later point it will be shown that comparison of the observed gas transfer ratios for pairs of gases and the available values of the diffusion coefficients are in agreement with this relationship.

The relationship indicated by equation (38) can also be readily developed by application of the liquid film theory of gas transfer. However, as indicated earlier, the concept of an imaginary stagnant liquid film, while it may be mathematically convenient, does not fit the physical facts, and hence has not been used here.

Effectiveness of Mixing and the Liquid Film.— The foregoing developments now permit a more specific analysis of the problem of imperfect mixing, and a more definite explanation of the related matter of the existence of a liquid film of finite thickness. Rearrangement of the terms of equation (35) indicates that

$$K = (D_m)(\frac{1}{D})(\frac{A}{V})(\frac{dc}{dr}) \quad (39)$$

and the two terms A and V now take on rather special meanings that relate specifically to the effectiveness of mixing. In the conceptual perfectly mixed system they would refer directly to the actual surface area of gas and water contact and to the whole volume of the system, and the value of $(\frac{V}{A})$ would properly be the actual depth of fluid. However, the actual mixing that occurs, both in laboratory experimental systems and in natural streams, is usually far from ideal, especially near the water surface. Instead, mixing is usually imperfect in the specific sense of partially separating the main body of fluid into regions within which the average rates of circulation and replacement of volume elements of water are somewhat different. Such regions may not have greatly different relative rates of circulation and therefore may not be obvious or distinct, but instead usually blend into each other. Thus, there is circulation and exchange of volume elements of water from one region to the other, but at a somewhat reduced rate than would be expected on the basis of the assumption of perfect mixing. In the usual case, one of the regions is most likely to consist of a relatively thin hydrodynamic water

layer near the water surface, and volume elements of water in this layer are physically not replaced by others from below with the freedom that the assumption of perfect mixing would imply. Under such circumstances, the actual rate of surface replacement will be lower than anticipated, and the observable bulk transfer coefficient, K, will also be lower. Also, the mean dissolved gas concentration gradients between neighboring volume elements of water will not be the same for the two regions of the whole system.

Thermal stratification of deep lakes and reservoirs offers a more extreme illustration of the occurrence of distinct regions within V. Under these circumstances there is very little exchange of volume elements of water between the epilimnion and the hypolimnion. Gas transfer across the interface between these two regions is therefore relatively very slow, with the result that dissolved oxygen concentration in the hypolimnion is demonstrably quite low relative to the epilimnion.

The occurrence of regions such as have been described will most often be difficult to demonstrate by usual methods such as random sampling for the average dissolved gas concentration. In particular, if the surface region is quite thin relative to the whole depth of fluid, the effect on the net gas transfer rate may be substantial even though the existence of the surface region may be virtually impossible to demonstrate experimentally. Such a region represents a surface "film" that has its origin in the hydrodynamic conditions. Gas transfer through it is slow because the rate of exchange of volume elements of water between the two regions is slow, and the degree of mixing and surface replacement that occurs within the upper region is considerably less than the simple assumption of perfect mixing would imply. In effect, imperfect mixing reduces the net rate of gas transfer below the rate that would occur if the whole system were perfectly mixed.

In any imperfectly mixed water system, which includes most experimental systems and most natural streams, the parameters A and V must therefore be regarded as the effective area and volume rather than directly measureable quantities. Alternatively, $(\frac{V}{A})$ may be regarded as an effective depth rather than the measureable depth. The important point is that in any imperfectly mixed system the direct application of measured values of area, volume and depth will create corresponding error in derived values of K.

Referring to equation (39), K is measurable under laboratory conditions, and so is the mean saturation deficit at any time. The numerical value of D_m may be taken as known (from the literature) for a specific system such as oxygen and water. It is clear, however, that the mean dissolved gas concentration gradient within V can never be independently measured or observed. If one could be certain that a system were perfectly mixed, then the value of the mean concentration gradient at any time could safely be calculated from equation (39), using observed values of K, D, A and V together with an accepted value for D_m. However, in any imperfectly mixed system, neither the effective volume or depth can be known independently any more than the value of $\frac{dc}{dr}$. Under such circumstances, only the product $(\frac{A}{V})(\frac{dc}{dr})$ can safely be evaluated.

Relation to Molecular Diameter.—Einstein's law of diffusion, developed from consideration of the Brownian motion, states that [2]

$$D_m = \frac{R\,T}{N_o f} \qquad (40)$$

where R is the universal gas constant, T is the temperature (° K), N_o is Avogadro's Number, f is the frictional coefficient and D_m is the diffusion coefficient. For spherical particles, Stokes' law indicates that

$$f = 6\pi\eta r \qquad (41)$$

where r is the radius of the sphere and η is the viscosity of the medium. Although these laws are thought to apply to particles of finite size rather than to molecules in most experimental situations, it appears from the evidence to be presented that they apply equally well for the case of molecules of gases transferring in water.

Combining (40) and (41), and applying the result to the experiment that involves the simultaneous transfer of two gases in water, it is found that

$$\frac{(D_m)_1}{(D_m)_2} = \frac{r_2}{r_1} \qquad (42)$$

which states that the ratio of diffusion coefficients of the two gases is inversely proportional to their molecular radii or diameters. Combining this result with equation (38), it is therefore seen that

$$\frac{K_1}{K_2} = \frac{(D_m)_1}{(D_m)_2} = \frac{d_2}{d_1} \qquad (43)$$

where d is the diameter of the gas molecules.

Equation (43) is the relation that was implied in the earlier paper on the open reactor experiments.[6] It appears to be a basic expression of the relationship between the volumetric transfer coefficient, K, the molecular diffusion coefficient, D_m, and the molecular diameter for dissolved gases. The experimental evidence in support of this relationship is presented in the following section of the report.

Experimental Verification

The gas transfer ratios observed in both the open and the closed reactor systems described earlier are analyzed here for purposes of testing as well as possible the foregoing developments regarding the mechanisms of gas transfer. In addition, a search of the available literature on gas transfer in stirred or agitated water and on the observed diffusivities of gases has been made, and the relevant results are also presented.

The relation between K_2 and water temperature has already been discussed, and the details need not be repeated here. The excellent agreement between the predicted value of θ, the temperature coefficient, and the value recently observed experimentally by Churchill et al. provides strong verification of the development of the basic reaeration equation, and, thus, of the nature of the exchange coefficient, K_2. This section of the report will therefore be devoted to analysis of the experimental evidence regarding the predicted relationship between K_2 and the molecular diameters of the gases tested, and to the evidence regarding the relationship between observed values of the diffusion coefficient and molecular size.

The literature contains no other experimental measurements of K_2 or of diffusivity that were obtained by simultaneous testing of pairs of gases, and this is unfortunate. In addition, the experimental systems used by the various investigators of gas transfer phenomena have differed in approach as well as in detail. As has been noted, the assumption of perfect mixing cannot safely be made for the various experimental systems that have been used, and, since neither mixing nor the rate of surface replacement can be independently measured, the assumption of identical mixing from one experiment to the next usually cannot be made. As a result, it is not usually possible to directly compare the gas transfer coefficients observed by different investigators. Only simultaneous testing of pairs of gases in the same experimental system can provide positive assurance that conditions of tubulent mixing and surface replacement were truly identical for purposes of comparing the absorption rates of the two gases, and only under such circumstances can the requirement of perfect mixing safely be eliminated. For this reason, although the literature contains some quantity of data on the absorption characteristics of various gases, the amount of data that is suitable for comparison to the results reported here is quite limited.

Relation of K_2 to Molecular Diameter.—In addition to the experimental results presented in this report for the simultaneous transfer of pairs of gases, two other sources have been found that permit comparison of the transfer capabilities of several gases in stirred or agitated volumes of water. These sources are the experiments of Hutchinson and Sherwood[3] and of Dobbins.[4] In each of these cases the investigators studied the bulk absorption rates of a number of gases under experimental conditions that appear to provide limited acceptable comparisons of the transfer rates of the several gases tested. The different gas absorption systems used by these investigators have been generally described at an earlier point, and these descriptions need not be repeated here. The reader is referred to the original published accounts of these works for further detail regarding the absorption systems and the results.

It should be noted also that, although both Hutchinson and Sherwood and Dobbins reported their observed gas absorption rates in terms of the liquid film coefficient, "k_L," what was actually measured in both cases was the bulk transfer coefficient, K_2. The liquid film coefficients that are reported are calculated rather than observed results, and are fictitious in that they require the assumption of perfect mixing ($K_2 = K_L \frac{A}{V}$) and in the sense described earlier. As has been noted, in both cases it appears quite doubtful that perfect mixing was actually achieved. However, comparison of the reported values of k_L in each case is still possible if it can be assumed that mixing and surface replacement were the same for practical purposes under specific standard test conditions. In that event, the ratio of actually observed K_2's would be the same as the ratio of reported "k_L's" for a pair of gases, as the effective depth ($\frac{V}{A}$) would be the same, and no assumption as to perfect mixing, instantaneous saturation, etc., need be made.

Thus, in the case of the Hutchinson and Sherwood data, the gas absorption rate coefficients obtained at the standard stirrer speed of 171 rpm have been used for purposes of comparing the transfer capabilities of pairs of gases. (Analysis of all of the Hutchinson and Sherwood data indicates that, at stirrer speeds below about 100 rpm and above about 500 rpm, a change in the relative degree of mixing and/or surface replacement prevents legitimate comparison of results obtained at high and low stirrer speeds with those for intermediate speeds.) The preliminary runs reported by Dobbins were all conducted with a lattice stroke of 2.5 cm, a speed of oscillation of 200 rpm, and a water cover over the lattice in its top position of 1.0 cm. Dobbins' more extensive tests with helium and nitrogen did not include these same conditions, but may be analyzed separately to provide the necessary information.

Review of the available literature regarding the molecular diameters of gases reveals good agreement in some cases and disagreement in others. The data contained in the Handbook of Chemistry and Physics [18] appear adequately to reflect both the agreements and the disagreements, and this appears to be the most appropriate source for these purposes. This source contains separate estimates of the molecular diameter for the individual gases based upon considerations of viscosity, Van der Waals' forces, and heat conductivity. In addition, for the nonreactive monatomic gases helium, krypton and radon, the covalent radii have been taken to be representative of the molecular size that is effective in gas transfer. The values of molecular diameter that have been used are given in Table VII.

TABLE VII.—Molecular diameters of gases*

Gas	Range	Covalent diameter	Diameter used
Oxygen	2.92–2.98	.....	2.95**
Hydrogen	2.32–2.40	.....	2.35**
Helium	1.90–2.65	1.86	1.90***
Nitrogen	3.15–3.53	.....	3.28**
Carbon dioxide	3.23–3.40	.....	3.32**
Krypton	3.14–3.69	3.78	3.69***
Radon	.....	4.28	4.28

*In Angstrom units.
**Mean value.
***Value nearest the covalent diameter.

Tables VIII and IX present the available experimental evidence regarding the inverse relationship between the bulk gas transfer coefficient, K_2, and the molecular diameter predicted by equation (43). Table VIII includes all of the gas transfer ratios that were observed directly in the simultaneous experiments using both the open and the closed reactors. For these pairs of gases, only the Hutchinson and Sherwood results include any comparative data and, in that case, only the combination carbon dioxide-oxygen is available.

Table VIII demonstrates excellent agreement between the observed gas transfer ratios and those predicted on the basis of the inverse relationship with molecular diameter given by equation (43). The only discrepancy worthy of note involves the krypton-to-helium ratio. In that case the observed ratio is in the predicted direction relative to the other ratios, but its numerical value deviates somewhat further from the predicted result than in the other cases. In view of the marked lack of agreement regarding the molecular diameter of helium (see Table VII), and in view of the general difficulty of handling that gas experimentally, the agreement between the observed and predicted krypton-to-helium ratios is regarded as quite good. The Hutchinson and Sherwood result for the carbon dioxide-to-oxygen ratio agrees fully with the results observed in the open reactor and with the predicted value. The mean krypton-to-oxygen ratio of 0.83 for both reactor systems agrees well with the separately observed values and with the predicted ratio of 0.80.

TABLE VIII.—Relation between K_2 and molecular size
[Direct observation]

	Gas transfer ratio		
		Observed (K_1/K_2)	
(Gas No. 1/Gas No. 2)	Predicted (d_2/d_1)	These studies	Hutchinson and Sherwood
a. Open reactor:			
(Kr/Oxy)	0.80	0.82	.....
(Rn/Oxy)	0.69	0.70	.....
(CO_2/Oxy)	0.89	0.89	0.91
b. Closed reactor:			
(Kr/Oxy)	0.80	0.85	.....
(Kr/Hydr)	0.64	0.59	.....
(Kr/Hel)	0.52	0.44	.....
(Kr/Nitr)	0.89	0.91	.....
(Kr/Kr)	1.00	0.99	.....

Table IX presents the further comparisons of observed and predicted gas transfer ratios that can be made using all of the data (these studies, Hutchinson and Sherwood, and Dobbins) and utilizing the relationship noted earlier:

$$\frac{\left(\frac{K_1}{K_2}\right)}{\left(\frac{K_1}{K_3}\right)} = \left(\frac{K_3}{K_2}\right) \qquad (44)$$

where the subscripts now identify three different gases. The ratios derived from equation (44) are referred to here as "indirectly observed" in order to distinguish them from the direct results obtained in the experiments that provided for simultaneous transfer of pairs of gases.

As noted before, all of the ratios derived from the Hutchinson and Sherwood data are for the standard stirrer speed of 171 rpm. The preliminary test data of Dobbins include seven reported values for the "k_L" of hydrogen, but the first two values listed (0.582 and 0.615) are clearly different statistically from the remaining five results (0.478–0.527); hence the first two results have been eliminated in order to obtain the best mean observed value for hydrogen. (The two high results may, for example, indicate the presence of a gas leak that was later eliminated or reduced.)

A representative observed value for the ratio of nitrogen and helium gas transfer coefficients had to be obtained by reanalysis of the Dobbins data, as no direct comparison of the observed values of "k_L" for the two gases under the same test conditions was presented. For this purpose, the observed data were taken from Dobbins' Figures 3 and 4 and were replotted on ordinary graph scales (rather than on semilog scales). Thus, for example, the observed values of "k_L" for nitrogen and for helium were plotted against stirrer speed on natural graph scales for a stroke of 2.5 cm and a cover of 0.0 cm. These analyses revealed that, in each case, the observed results were best fitted by a single straight line at the lower speeds of lattice oscillation, that a transition occurred at an intermediate rpm, and that the results at higher speeds were considerably more erratic but were best described by a second much steeper straight line. This appears to be the same phenomenon shown earlier in Figure 14, and indicates a change in the relationship between rpm and the rate of surface replacement, or a change in the efficiency of surface replacement by mixing or agitation. For the case cited above (stroke of 2.5 cm and 0.0 cm cover) this transition occurred at a lattice oscillation speed of 120–150 rpm.

TABLE IX.—Relation between K_2 and molecular size
[Indirectly observed]

(Gas No. 1/ Gas No. 2)	Gas transfer ratio: Predicted (d_2/d_1)	Observed (K_1/K_2): These studies	Observed (K_1/K_2): Hutchinson[1] and Sherwood	Observed (K_1/K_2): Dobbins
(Hydr/Oxy)	1.26	1.41	1.27	1.42**
(Hel/Oxy	1.55	1.88	1.30	2.04
(Nitr/Oxy)	0.90	0.91	0.87	0.94
(Hel/Hydr)	1.24	1.34	1.02	1.43
(Nitr/Hel)	0.58	0.49	0.67	0.46***
(CO_2/Hel)	0.57	0.47	0.70	....
(Rn/Hel)	0.44	0.37	.....	....
(Nitr/Hydr)	0.72	0.65	0.69	0.66
(CO_2/Hydr)	0.71	0.63	0.72	....
(Rn/Hydr)	0.55	0.50	.....	....
(CO_2/Nitr)	0.99	0.98	1.04	....
(Rn/Nitr)	0.77	0.77	.....	....
(CO_2/Kr)	1.11	1.07	.....	....
(CO_2/Rn)	1.29	1.27	.....	....
(Kr/Rn)	1.16	1.18	.....	....

*All at 171 rpm.
**Eliminating the 1st 2 of 7 results for hydrogen (see text).
***Based on reanalysis of observed data (see text).

In each case involving a particular combination of stroke and cover, individual values of the nitrogen-to-helium ratio of observed "k_L's" were evaluated for those lattice speeds that were lower than the speed associated with the transition to a steeper slope. The individual ratios thus obtained were constant for each condition of stroke and cover, and were clearly independent of lattice oscillation speed. Their average value was 0.46, as shown in Table IX.

The results presented in Table IX again clearly demonstrate the inverse relationship between K_2 and molecular size. With the single exception of the ratios that involve helium, the agreement between the predicted ratios and those observed in the several studies is very good. The observed ratios involving helium again are in the predicted direction relative to the other ratios, but the predicted and observed ratios differ numerically somewhat more than is the case for the other gases. The agreement between the values observed in these studies and in the studies of Dobbins is excellent, but the Hutchinson and Sherwood results involving helium appear different. Although the underlying cause of the difference between predicted and observed ratios involving helium cannot be known with certainty, the results presented in Tables VIII and IX, taken collectively, hint that the estimated molecular diameter of helium of 1.90 angstrom units may be too large. Thus, an effective molecular diameter for

helium of 1.65 or 1.70 angstroms, instead of 1.90, would bring all of the predicted ratios involving helium into very good agreement with the observed results.

The results presented in Tables VIII and IX constitute strong experimental verification of the inverse relationship between K_2 and molecular diameter presented in equation (43) and in the earlier paper on the open reactor studies,[6] and for the gases shown in the tables that relationship is regarded as fully demonstrated. This also implies clearly that the escape coefficient, b, contained in equation (32) is inversely proportional to the molecular diameter of the transferring gas.

Relationship of Diffusivity to Molecular Diameter.—A considerable quantity of data appears to be available regarding the molecular diffusion coefficient, D_m, for various gases in water, and at first glance it appears that suitable ratios of D_m should be obtainable for most of the gases referred to in Tables VIII and IX. Unfortunately, a more thorough review of the available information indicates that this is not the case. Indiscriminate application of the available data could be used, and suitable references cited, either to "prove" or to "disprove" the inverse relationship between D_m and molecular diameter that is predicted by equation (43), and it is therefore necessary to interpret the available data with caution. To quote Himmelblau: [19] "A shortage of reliable diffusion data exists which makes it difficult to evaluate proposed correlations for diffusivity or determine the effect of temperature, pressure, concentration, etc., on diffusivity."

At least six different experimental systems have been designed and used for measurement of the diffusivity of gases in water, and these have been critically reviewed by Himmelblau.[19] Other techniques are noted and reviewed by Vivian and King [20] and by Davidson and Cullen.[21] The several techniques do not all provide comparable results, especially in that some involve gas transfer from the gas to the liquid phase while others do not. According to the above sources, differences in observed values of D_m are to be expected as the result of such differences in the experimental systems used. As noted earlier in this report, true Fickian diffusion refers to the transfer of molecules of dissolved substance within a single medium, rather than to transfer from one medium to another such as from gas to liquid. The problem of comparing observed values of the diffusion coefficient is further complicated by the fact that the individual observations have been made over a wide range of temperatures, and this necessitates conversions that may not be accurate. As a result, the comparisons that can safely be made are quite limited. They are presented in Table X, in terms of the ratio of the diffusivity of the second gas to that of oxygen.

Referring to Table X, the diffusion coefficients for oxygen and for carbon dioxide appear from the literature to be firmly established, and are taken to be 2.1 and 1.8×10^{-5} cm^2/sec, respectively, at 20° C. The diffusivity of nitrogen also appears to be reasonably firm at 1.9×10^{-5} cm^2/sec, at the same temperature. A wide range of diffusion coefficient has been reported for the light gases helium and hydrogen, and it appears impossible to justify the selection of a single result, or of the simple arithmetic mean value, as best. Accordingly, only the range of ratios is shown for these light gases in Table X. No observed values have been found for the diffusivities of radon or krypton.

TABLE X.—Relation between diffusivity and molecular size
[20° C.]

Gas	Predicted ratio (d_{ox}/d_{gas})	Observed ratio $(D_m)_{gas}/(D_m)_{ox}$
Carbon dioxide	0.89	0.86
Nitrogen	0.90	0.91
Hydrogen	1.26	(1.4–4.2)
Helium	1.55	(2.0–4.3)

As a result of the foregoing difficulties, the results presented in Table X provide by themselves only limited experimental verification of the inverse relationship between diffusivity and molecular size predicted in equation (43). The carbon dioxide-to-oxygen and the nitrogen-to-oxygen ratios of diffusivity agree excellently with the predicted ratios and with the observed results shown in Tables VIII and IX. For the light gases, the comparison is less clear. In each case (helium and hydrogen) the lowest value of the ratio of observed diffusivities agrees excellently with the observed ratios of K_2 values shown in Table IX, and reasonably well with the predicted ratio. These gases are quite difficult to handle experimentally, gas leaks being particularly difficult to control, and the presence of leaks would lead to too high an observed diffusivity. However, although the collective experimental evidence indicates the likelihood, it cannot be conclusively demonstrated that the lowest observed diffusivities

(2.9×10^{-5} cm²/sec for hydrogen and 4.2×10^{-5} cm²/sec for helium, at 20° C.) are the best values. The comparisons presented in Table X, coupled with the comparable observed results in Tables VIII and IX, thus provide reasonable but not conclusive experimental support of the prediction of equation (43) concerning diffusivity and the molecular diameter. The available data on the diffusivity of the various gases in water are too limited and disagree among themselves to too great an extent to permit any more firm conclusion. This in no way detracts, however, from the firm experimental verification that has been presented concerning the inverse relationship between K_2 and the molecular diameter.

Derived Estimates of Diffusivity

As indicated above, reliable values of the diffusion coefficient, D_m, are not available for most gases diffusing in water. Furthermore, the diversity of experimental approaches to measuring the diffusivity of gases in water indicates that this situation is not likely to improve greatly very soon. However, the diffusion coefficients for a few gases, notably carbon dioxide and oxygen, do appear to be reasonably firm, and the relationships expressed in equation (43) provide a useful means of extending the list of estimated values. Thus, if the diffusion coefficient is regarded as known for one gas and the molecular diameters are known for it and another gas, the diffusion coefficient for the second gas can be estimated by use of equation (43), at a common temperature. For instance, taking the diffusion coefficient of oxygen to be 2.1×10^{-5} cm²/sec at 20° C., the pertinent ratio of molecular diameters (see Table IX) indicates that the diffusion coefficient for hydrogen at the same temperature should be about 2.7×10^{-5} cm²/sec. However, the observed ratios of K_2 values for hydrogen and oxygen shown in Table IX probably provide a more accurate conversion in this case, and would lead to a diffusion coefficient for hydrogen of 3.0×10^{-5} cm²/sec at 20° C. Other gaseous diffusion coefficients can be estimated similarly.

field tracer measurement of reaeration

CHAPTER FOUR

INTRODUCTION

This section of the report describes in detail the tracer technique that has been developed for evaluation of natural stream reaeration capacity, including the experimental basis, the field methods, and the demonstration studies of reaeration of the Jackson River, Va. As indicated earlier, field application of the tracer technique involves the use of three tracers, namely, tritiated water, dissolved krypton-85, and a fluorescent dye. For the river reach covered, and at the prevailing flow, the tracer study provides direct evaluation of the gas exchange capacity, time of flow, and dispersion, both total and longitudinal.

To recapitulate briefly, the fluorescent dye yields time of flow and longitudinal dispersion information for the reach, and also indicates when to sample for the other two tracers; the tritiated water provides an accurate measure of the total dispersion; the dissolved tracer gas is dispersed to the same extent as the tritiated water, and, in addition, is lost to the atmosphere as the result of turbulent mixing and surface replacement. The change in concentration of the dissolved tracer gas between two sampling points, relative to the change in concentration of tritium, indicates the percent of dissolved gas that has been lost within the reach, as shown below. This is then converted to the exchange capacity for oxygen by use of the known krypton-85 : oxygen ratio whose basis was shown in Chapter II. The tracer method assumes essentially that the concentration of tritiated water changes within the reach only as the result of dispersion, that the krypton-85 concentration changes additionally only because of loss to the atmosphere, and that the ratio of K_2 values for krypton-85 and oxygen is a constant (0.83) that is not significantly affected by temperature, turbulence or usual concentrations of water pollutants, within the range of interest.

The field tracer technique for evaluation of stream gas exchange capacity employs the same device of simultaneity that was used in the laboratory, in order to avoid the many problems and the many sources of significant error associated with any attempt to independently evaluate turbulence or the rate of surface replacement. Thus, the three tracers are released as a single, simultaneous dose, and, in addition, the concentrations of both tritium and krypton-85 are subsequently measured simultaneously in any single river sample. As a result of these methods, the gas exchange capacity can be evaluated accurately by the use of an instantaneous point dose and by subsequent point sampling. A uniform cross-sectional dose

(essentially impossible to achieve in a practical situation) is not required, and it is not necessary to attempt to perform an accurate tracer mass balance. As will be shown, the device of simultaneity thus makes the task of evaluating stream reaeration capacity both much simpler and much more accurate than is possible otherwise.

The field tracer technique described here was first applied in several reaches of the Little Miami River near Cincinnati, Ohio, in the spring and early summer of 1966. The purposes of those studies were primarily developmental, and they served as a means of testing and perfecting the various field methods (dose preparation, dosing, sampling, sample counting) and of field testing all equipment. Several releases were made, at flows of about 150 c.f.s. for these purposes. The subsequent full scale field demonstration of the tracer technique was conducted in the Jackson River, between Covington and Clifton Forge, Va., at flows of about 100 c.f.s. The Little Miami River reaches studied were moderately to lightly polluted, whereas the Jackson River below Covington was heavily polluted with papermill wastes.

Smaller streams were selected for the first field trials of the tracer method for the sake of simplicity, in that they could be waded in most locations, and especially in that the quantities of radioactive tracers to be handled could be minimized at first. Also, both streams had a preponderance of shallow, relatively rapid reaches, so that significant gas losses could be expected within relatively short distances. The highly efficient sample counting methods that were devised for these studies also were of great assistance in minimizing the quantities of radioactive tracers required, to the extent that it proved quite acceptable to prepare the dose and release it in the stream directly, without public radiation hazard and without significant radiation dose to the study personnel. The quantities of tracer required will be proportional to the quantity of river flow, other conditions being equal, and although the public exposure to radioactivity need not be increased accordingly, the radiation dose received by survey personnel dosing larger river flows could become unacceptable without the use of shielding. Thus, at flows much above about 200 c.f.s. other somewhat more cumbersome dosing techniques will be required. The studies in the Little Miami and the Jackson Rivers were reviewed and approved by the U.S. Atomic Energy Commission, and a license for them issued by that Agency, and they were also approved by the responsible State agency in each case.

EXPERIMENTAL BASIS

Let A and B represent two points along the course of a stream, A being the upstream location. A single homogeneous solution containing the three tracers referred to above is released at point A; this dosing solution is released into the main flow of the stream instantaneously, and is subsequently dispersed laterally, vertically and longitudinally. A continuous flow recording fluorometer samples the main river flow at B and records dye concentration as a function of time. River water samples are collected at B at frequent intervals as the dye peak approaches and passes B, and these samples are subsequently analyzed for the concentrations of krypton-85 and tritium.

Let zero time be the moment at which the tracer dose solution was released at A, and let t be the time at which the dye peak passes the sampling point B. Let N_K be the number of atoms of krypton-85 and N_T the number of atoms of tritium originally released at A, and let C_K and C_T be the respective concentrations of krypton-85 and tritium, in atoms per liter, observed in the sample taken at B at the peak dye concentration. Then

$$\left(\frac{N_K}{N_T}\right)$$

is the number of atoms of krypton-85 per atom of tritium dosed at A, and

$$\left(\frac{C_K}{C_T}\right)$$

is the number of atoms of krypton-85 per atom of tritium remaining at B. The fraction of krypton-85 atoms that remain dissolved at B is therefore just

$$\frac{\left(\frac{C_K}{C_T}\right)}{\left(\frac{N_K}{N_T}\right)} = f_K$$

and the decimal percent of atoms of krypton-85 that has been lost to the atmosphere within the reach is

$$\frac{\left(\frac{N_K}{N_T}\right) - \left(\frac{C_K}{C_T}\right)}{\left(\frac{N_K}{N_T}\right)} = (1 - f_K)$$

In accordance with the basic expression for gas exchange, the fraction of krypton-85 atoms remaining at B is also

$$f_K = e^{-K_{Kr}t}$$

and it is also known that the fraction of the initial dissolved oxygen saturation deficit remaining unsatisfied at B is

$$f_O = e^{-K_{Ox}t}$$

Combining the above two expressions, and setting $K_{Kr} = 0.83\ K_{Ox}$ as found in the laboratory studies, it may be shown that

$$\log (f_O) = \frac{\log (f_K)}{0.83}$$

Thus a field determination of the fraction of krypton-85 atoms remaining at B is readily converted to an evaluation of the fraction of the initial dissolved oxygen deficit that remains unsatisfied at B. As has been shown, the fraction of krypton-85 atoms remaining dissolved at B is just the ratio of krypton-85 : tritium concentrations at B divided by the ratio of krypton-85 : tritium atoms in the dosing solution released at A. Similarly, if an additional sampling point, C, is located downstream from B, it is readily shown that

$$f_K = \frac{(\frac{C_K}{C_T})_C}{(\frac{C_K}{C_T})_B} = e^{-K_{Kr}t}$$

for the river reach between points B and C, and where t is now the time of flow between B and C.

The procedures that have been developed incorporate simultaneous counting of the field samples for their concentrations of krypton-85 and tritium. The ratios $(\frac{C_K}{C_T})$ are thus determined for the individual field samples for use in the last expression.

It is apparent from the last expression given above that the numerical value of K_{Kr} can be easily and accurately obtained by a simple graphical procedure: If the observed values of $(\frac{C_K}{C_T})$ for the two sampling points are plotted on the logarithmic scale of a sheet of semilog paper and separated by the time of flow between B and C, the slope of the resulting straight line will be the observed value of K_{Kr}. This may then be converted directly to the desired K_{Ox} by dividing it by 0.83. Alternatively, the observed value of K_{Kr} may be calculated directly from the last expression given above.

The notion of an instantaneous dose was introduced for the sake of simplicity in regard to the foregoing developments. It is clear, however, that this is not a necessary condition, as the observed value of K_{Kr} is determined by the use of concentration ratios rather than by the use of absolute concentrations. In the same sense, it is not really necessary to determine the individual absolute concentrations of krypton-85 and tritium, even though the counting procedures that have been developed do so. Rather, the only necessary condition is that the efficiencies of counting be the same for samples taken at the two locations.

As noted earlier, it cannot be assumed that there is truly a single value of K_{Kr} or K_{Ox} for a natural river reach of practical length. The gas exchange capacities determined by the tracer procedure thus represent averages rather than single true values of K_2. As they are the result of direct measurement, they reflect the real conditions of imperfect turbulent mixing and surface water replacement that occurred in the river reach tested, under the prevailing conditions of flow, depth, temperature, weather, etc.

FIELD AND LABORATORY PROCEDURES

The field and laboratory procedures described here were designed for the purpose of evaluating the reaeration characteristics of, say, 10 to 20 miles of free-flowing inland stream at flows up to 200–250 c.f.s., from a point of pollution through the critical zone of the oxygen sag and well into the recovery zone. In particular, these procedures were developed with the specific aim of obtaining maximum information from minimum tracer releases, and represent a balance of sensitivity, safety and cost for streams of this size and type. For greater flows, major impoundments and tidal estuaries, modification of the procedures in one detail or another will be necessary for personnel protection against excessive radiation dose, representative sampling and adequate interpretation of field results.

The final field procedure, in brief, consisted of dividing the main reach to be studied into a number of subreaches, defined by the sampling stations, and of releasing a series of tracer doses at successive downstream locations. The dose release points were selected so as to provide at least

double coverage of each subreach, for purposes of accuracy and in order to test the reproducibility of derived values of K_{Kr}. The releases were sufficiently separated in time (usually two days) so as not to overlap at any sampling station. The river was cross-sectioned prior to the first tracer release as an aid to selection of sampling stations and in order to obtain physical data for subsequent analysis. In the Jackson River studies, a series of eight separate releases was made, covering 15 subreaches that averaged about 1.2 miles each in length.

Dose Preparation

The three tracers are originally procured in somewhat different forms, and require preliminary treatment in order to prepare a single homogeneous mixture for dosing. The fluorescent dye used in these studies was rhodamine-WT, obtained as a 20 percent aqueous solution. The tritium was obtained directly as tritiated water in small vials containing about 500 mc of tritium in 25 ml of water. The krypton-85 was obtained as a powdered kryptonate in small water-soluble capsules. In this form, the krypton-85 atoms are attached to a hydroquinone that dissolves readily on contact with moisture and releases the krypton gas. For the field studies reported here, capsules each containing about 100 mc of krypton-85 were procured and used. Considerable difficulty was encountered in obtaining the quantities of radioactive tracers that were ordered, as the assays by the suppliers were grossly inaccurate, and it was necessary to assay each dosing solution independently for accurate results.

Successful application of the field tracer method requires that the krypton-85 be fully in the dissolved state in the dosing solution, otherwise inaccurate results may be obtained. Careful preparation of a true water solution of the tracer gas is therefore the most sensitive and important aspect of dose preparation. For the earlier laboratory studies in the open reactor,[6] krypton-85 gas was initially dissolved directly into the circulating water, but the larger quantities of tracer required for the field operations make this method relatively cumbersome and unsafe, and the kryptonates proved to be considerably simpler to use.

Each dose was prepared immediately prior to field use. The first step in the procedure was to dissolve the krypton-85 in distilled water, and this was carried out in an exhaust hood in a nearby laboratory. The procedure was as follows: A 1-liter bottle with a ground glass stopper was filled with degassified distilled water at room temperature, and a magnetic stirrer placed in the bottle; the desired number of kryptonate capsules was then dropped into the water and the bottle immediately sealed with its stopper; the water was then stirred vigorously by means of the magnetic stirrer until the released krypton-85 was dissolved, a period of 2 hours or so. This entire procedure was conducted behind a shield of 2-inch lead bricks. The water-soluble capsules containing the powdered kryptonate were very thin-walled, and dissolved within a few seconds after being placed in the water. A bubble, consisting mainly of the air originally contained in the capsules, was then seen in vortex form at the top of the bottle. Usually this bubble disappeared completely by the end of the stirring period, but occasionally it did not. Any krypton-85 contained in the bubble was, of course, vented and lost when the bottle was opened at the end of the stirring period. In either circumstance, subsequent assay of the dosing solution indicated that most (better than 90 percent) of the krypton-85 was dissolved by the procedure.

After the dissolving period, and before mixing with the other tracers, a 1-ml aliquot of the krypton-85 solution was taken and diluted to 2 liters for subsequent separate assay of the krypton-85 dose. The several small vials containing about 25-ml each of tritiated water required for the whole dose were also diluted to a total of 500-ml in a separate vessel, and a 1-ml portion of that mixture was taken and diluted to 2 liters for the separate and independent assay of the tritium dose. These individual assays of the two radiotracer doses were later compared to the separate simultaneous assay of both tracers obtained from a sample of the mixed dosing solution, to provide verification of the final dose released to the stream.

The field dosing container was a 4-liter glass vessel with a thick plastic cover that could be sealed onto the container with a quick-release type clamp. The flat cover contained an opening with a fitted stopper to facilitate taking a sample of the dosing mixture. The desired quantity of dye (2 liters for the Jackson River studies) was placed in the dosing container and a magnetic stirrer added. The dosing container was then placed in the exhaust hood, and the 500-ml solution of tritiated water added. The initially prepared 1-liter solution of tracer gas then was transferred to the dosing container by use of a

siphon, and was added well underneath the surface of the dye solution. The remaining space in the dosing container was then filled with degassified distilled water, the cover was clamped in place, and the stirrer started at a medium speed to assure a homogeneous mixture of the tracers. This mixture was transported to the field dosing station immediately before use.

Radiation Safety.—The beta emission from tritium is weak and is therefore absorbed in the solution and the walls of the dosing container, so that no detectable personnel radiation dose resulted from the tritium. The beta emission from krypton-85 is more energetic, however, and also some penetrating gamma radiation is present. Hence, care must be exercised to minimize the radiation dose received by personnel handling this radioisotope. As noted, the laboratory dose preparation was carried out behind lead bricks to reduce this radiation dose. A radiation survey meter connected to a loudspeaker was also used in the laboratory as one means of monitoring and as a warning device. In addition, the personnel handling the radioisotopes wore pocket radiation dosimeters and film badges for purposes of measuring the radiation dose actually received.

Field release of the tracer solution involved brief direct handling of the dosing container, and was therefore another source of personnel radiation exposure. As a further precaution, therefore, the individuals who handled and released the dosing solution in the field were usually different from those who prepared the dose, even though this was not required by the strength of the radiation dose involved. The field procedure required that the dosing solution be sampled immediately prior to release; immediately following that, one individual waded with the dosing container to the main channel of stream flow and released the dose at once into the main stream flow. This required that individual to handle the dosing container directly for 3 to 4 minutes. Prior monitoring of the filled dosing container demonstrated that the dose received during this brief exposure was quite small.

As a result of these and other precautions, in no case did the external radiation dose received by an individual approach the daily limit that is allowed for continuous occupational exposure over a lifetime. The personnel involved were actually exposed to radiation only a small number of times on a brief, intermittent basis, so that the radiation dose received was quite insignificant.

The quantities of krypton-85 and tritium released were also completely insignificant in terms of any public radiation hazard. No significant use of either the Little Miami or the Jackson Rivers occurred for many miles below the study areas, although an occasional fisherman was observed in the upper reaches of the Little Miami. The river concentrations of krypton-85 and tritium were below the maximum permissible concentrations for continuous lifetime exposure of the public within 100 to 200 yards of the release point, so that no public hazard was involved in any event.

The use of the field tracer method for evaluating stream reaeration capacity in much larger flows need not result in any additional public exposure hazard, as the actual stream concentrations need be no larger than those that were obtained in these studies. However, the quantities of tracer to be released will have to be larger, roughly in proportion to the flow, and beyond the tracer doses required for 200–250 c.f.s. of flow, further precautions will be necessary for the protection of survey personnel who prepare and release the tracer dose, particularly the latter.

Field Procedures

Detailed plans for the Jackson River study field operations were based upon available information regarding the prevailing D.O. profile below Covington, Va., an initial field reconnaissance, and an initial dye release. The study period, late July, 1966, was selected to correspond to a period of critically low stream flow. Prior stream cross-sectioning and concurrent stream oxygen balance studies were conducted by others for the Chesapeake Project of the Federal Water Pollution Control Administration. Separate reports of those associated studies are available, and the details will not be repeated here.

The Jackson River between Covington and Clifton Forge, Va., is a relatively wide and shallow stream, with a variety of both rapids and pooled sections. The principal sources of organic pollution are the treated watstes from the West Viginia Pulp & Paper Co. mill at Covington and the wastes from the community of Covington. At the time of the studies reported here, secondary treatment units at the papermill were out of operation. The D.O. profile below Covington dropped sharply to zero D.O., remained at the zero level for several miles, and then began to recover midway between Covington and Clifton Forge. At about the midpoint of the study period,

the secondary treatment units at the paper mill were placed back in operation, and the D.O. profile improved substantially and quickly.

Study Plan.—The detailed study plan envisioned the use of two separate field crews (two members to each crew) operating separate fluorometers and leapfrogging each other to provide adequate coverage of alternate sampling stations below the point of any tracer release. The river was divided into 15 subreaches, averaging 1.2 miles each in length, with dye monitoring and sampling locations at the ends of each subreach. The individual tracer release operation consisted of releasing the dose and following it as far as possible, as indicated by the dye measurements. Usually four subreaches were covered by a single tracer release, and one field crew would monitor and sample at the first and third stations while the other handled the second and fourth stations. The next tracer release, usually 2 days later, might be made at the second or third station of the prior release, and the eight tracer releases were thus staggered in location proceeding downstream. A total of six releases was initially planned, but it proved advantageous to add two releases at the end of the study period.

The stream sampling stations were selected as well as possible for their accessibility with the field equipment, their relation to the prevailing D.O. profile, the estimated time of flow below the next upstream station, etc. The field equipment, consisting of the fluorometer, portable gasoline-powered generator, submersible pump, hose, sample containers, etc., required that the sampling stations be reasonably accessible to field vehicles, but this did not create major difficulty in selecting stations.

The liquid scintillation counter to be used for counting the krypton-85 and the tritium content of the field samples could not be moved from its base location at Cincinnati; hence the study plan included packaging and shipping the field samples to Cincinnati for analysis. Sample preparation and counting methods permitted prompt analysis, however, and the individual tracer studies were scheduled so as to facilitate immediate delivery of the samples by bus to the Cincinnati laboratory. The usual schedule involved closing down the fourth field sampling station in time to place the entire set of samples on a late bus due to arrive in Cincinnati at about 8 a.m. the following morning; the bus was met by the laboratory personnel, the samples taken to the laboratory for immediate preparation, and the prepared samples were generally in the counter by noon or shortly thereafter. Counting, sample changing and recording of the individual sample counts were automatic, and thus could continue overnight. As a result, most of the data could be transmitted by telephone the next morning (about 48 hours after the tracer release) to the Virginia headquarters. This permitted the field study group to stay aware of the field results and facilitated control of the field studies. Had this procedure not been followed, the field study staff would not have realized until much later that the assays provided with the purchased radiotracers were highly inaccurate, and several of the scheduled tracer releases would undoubtedly have been inadequate.

Initial Dye Release.—For purposes of field testing the fluorometers and their associated equipment, and principally as the best means of estimating the required minimum tracer releases, 1 liter of rhodamine-WT dye was released below Covington before using the radiotracers. This test revealed some interference with detection of the dye by the colored papermill effluents, and necessitated the use of 2 liters of dye in each of the subsequent tracer doses. Fluorometers located at the first two downstream sampling points also provided estimates of the degree to which the dye had been diluted and dispersed by the stream flow, and this permitted good estimates to be made of the minimum quantities of radiotracers that would be needed for detection through four subreaches.

Dose Release and Assay.—The usual tracer release was in the early morning hours, between 3 a.m. and 6 a.m., and the usual dose was followed in the stream for approximately 16 hours time of flow through the four subreaches, or for about 5 miles. The previously prepared dosing mixture was transported to the stream dosing point by vehicle, together with a previously prepared 1-liter ground glass-stoppered bottle (containing a magnetic stirrer bar) filled with degassified distilled water. At the dosing point, the stopper was removed from the cover of the dose container, and a 2-ml portion of the mixed dose was taken and transferred into the one-liter dilution bottle. The dilution bottle was immediately stoppered and stored for subsequent assay of the mixed dose. The dose container was also restoppered at once, and was then taken without further delay to midchannel by wading, where the mixed dose was released into the main stream flow. The exact time of the release was noted in

the fieldbook, and this completed the dosing operation.

Field Sampling.—One of the field sampling crews was usually beginning to set up the equipment and place it in operation at the first downstream sampling station at about the time of the tracer release. After completing the dosing operation, the dosing party also proceeded to the first field sampling station to provide any necessary assistance. Time of flow to the first sampling station was usually 3 hours or so. Once the first station was in operation, the dosing crew left.

The field dye monitoring and sampling arrangement consisted of placing a submersible pump in the main stream flow at a shallow section, and delivering the pump outflow through a length of hose to a continuous flow recording fluorometer located at the edge of the stream. The pump and fluorometer were operated with power from a portable gasoline-powered generator. After passing through the fluorometer for measurement of dye concentration, the pump flow was split, the major portion going to waste and a smaller flow being delivered to a glass 25-ml sampling bottle via transparent flexible plastic tubing. This flow was delivered at the bottom of the sample bottle at a slow rate, so as to avoid any losses of the tracer gas. The flow was allowed to spill over the top of the sample bottle until a sample was wanted. All sample bottles were numbered for identification, and each was equipped with a correspondingly numbered pressure type screw cap.

The fluorometer dial and recording chart were watched for the start of the leading edge of the approaching dye mass, and the chart was marked occasionally with the correct time. Sampling was begun soon after the presence of the dye mass established, and was continued at an increasing frequency as the peak dye concentration approached the station. The time and identification number of each 25-ml sample were noted both on the fluorometer recording tape and in the field notebook. Each sample was pressure-capped at once, sealed for shipment with black plastic tape, and placed in a wire rack for transport to the field laboratory. As the dye peak passed the sampling station, the frequency of sampling was decreased. The dye curve was followed, and intermittent sampling continued, until the observed dye concentration diminished to about half of the peak concentration. At this point sampling was discontinued and the equipment was dismantled and loaded into the field vehicle for movement to the third sampling station.

The same procedure was followed at all sampling stations. The second crew placed station number 2 in operation well in advance of the presence of dye, followed the same sampling procedure as outlined above, and moved to the fourth sampling station upon completion of sampling at station 2. At the end of the sampling period for the fourth station, samples around the peak dye concentration were selected from each of the station sets, packaged for shipment, and delivered to the bus for transportation to the Cincinnati laboratory.

A third fluorometer had been calibrated with known dye solutions and was kept in the field laboratory. On completion of sampling for each tracer release, some of the field samples were analyzed for true dye concentration by use of this third fluorometer, to thus calibrate the dye curves observed at the field sampling stations.

Laboratory Procedures

Over a period of almost 2 years prior to the field studies reported here, a number of different procedures for counting krypton-85 in water samples were developed and tested in the laboratory. The purpose of this work was to develop and perfect a counting method having maximum efficiency, in order to minimize the quantity of krypton-85 required for field use. This would not only reduce the costs of the field operations, but, even more important, would reduce and minimize the occupational and public radiation hazards involved. The several procedures that were developed and tested included direct counting of a water solution of krypton-85 in a flow-through Geiger tube,[6] direct counting of small water samples in a low background anticoincidence-beta counter, submersion of a waterproofed Geiger tube in the solution to be counted, direct counting in the gaseous state after stripping the krypton-85 from solution, and direct liquid scintillation counting of the water solution of krypton-85. The details of these studies have been reported elsewhere,[25, 26] and will not be repeated here.

Tritium has only a weak beta emission, and liquid scintillation counting is a necessity for obtaining acceptable counting efficiencies. This method also proved to be by far the most efficient means of counting krypton-85. The energy of the beta emission from krypton-85 is considerably greater than that from tritium, and this made it feasible to develop a procedure for simultaneous

counting of both radiotracers in a single water sample.

The method finally perfected and used for the field studies involved direct simultaneous counting of krypton-85 and tritium in replicate 2-ml portions, using a 3-channel Packard TriCarb liquid scintillation counter equipped with an automatic sample changer and a count printout system. The counter was also equipped with a standard radiation source that could be used to provide a specific counting efficiency for each sample counted, and the counter could be preset for total count (on which it printed out the elapsed time of counting) or total time (on which it printed out the total count). The presence of sample impurities such as the dye caused some reduction of counting efficiency (by "quenching"), and calibration curves were prepared for the individual and mixed radiotracers with and without the presence of the dye. For a mixed sample, the channel energy limits were set so that tritium counts were recorded only in the lowest energy channel (channel A) and krypton-85 counts were recorded primarily (about 88 percent) in the higher energy channel (channel B). The fraction of krypton-85 counts that "spilled over" into channel A was known from the calibration curves, for any sample. The third channel (channel C) was reserved for recording the standard source count associated with each sample.

For each tracer release, the headquarters laboratory received for analysis a set of three river samples taken at and near the peaks of each of the four sampling station dye curves, a set of background samples taken at each station well before the dye mass reached the station, and a complete set of dose samples. All of these samples were in the pressure-capped 25-ml bottles. Preparation of all samples for counting was systematically from "cold" to "hot," to avoid any possibility of significant cross-contamination of samples. Thus, the background set was prepared first, the samples for station number 4 were set up next, station 3 next, and so on, the dose samples being prepared last.

Preparation of the individual samples for counting consisted of transferring a 2-ml aliquot from the 25-ml sample bottle to a 25-ml counting vial; the counting vial was then filled full with Butler's solution containing the liquid scintillator, capped, and set aside for subsequent counting. The procedures for transferring a 2-ml sample portion to the counting vial and for adding the scintillator solution were carefully designed to prevent any loss of the dissolved krypton-85.[26] For each sample, three replicate 2-ml portions were thus prepared for counting. Also, the liquid scintillation counter was equipped for automatic recycling of the counting vials, and the procedure developed included counting each vial at least twice. Thus, for each sample a total of at least six separate counts was available, each of three replicate portions being counted at least twice. The standard counting period for the river samples was 20 minutes, so that a minimum of 120 minutes of total counting time was provided for each sample. Three samples were counted in this way for each river sampling station. This procedure, involving considerable replication and long total counts, provided excellent counting statistics, and a high level of accuracy for river samples whose count rates might be in the neighborhood of only twice the background count rate.

The diluted dose samples were much more radioactive than the river samples, hence excellent counting statistics were attainable in much shorter counting periods by the use of the preset count procedure.

Usual counting efficiencies obtained by the liquid scintillation counting procedure were about 11 percent for tritium and 55 percent for krypton-85 in the river water samples, and slightly higher for the separate tritium and krypton-85 dose samples. The mixed dose samples, containing a substantial dye concentration, had somewhat lower counting efficiencies, a typical set being about 8 percent for tritium and 50 percent for krypton-85. The overall sensitivity of the sample counting procedures thus permitted the field use of minimal tracer quantities, particularly krypton-85, and detection and counting of the tracers at relatively quiet low river water concentrations.

Analysis of Counting Data

Typical counting data, taken from the results for Dump No. 14 (see the following section on the Jackson River studies), will be used here as an example of the methods of data analysis and interpretation.

Dose Calculations.—As noted earlier, three separate dose samples were taken for counting, specifically, separate tritium and krypton-85 doses without dye and a mixed dose sample that contained all three tracers and was collected from the dose container immediately before the dump was made.

The separate tritium dose sample had the fol-

lowing treatment: In the field laboratory, four small vials of tritiated water (about 25-ml each) were diluted up to 500 ml, and a 1-ml portion of that mixture was then diluted to 2 liters; samples of this latter solution were shipped to the Cincinnati laboratory for counting, and three replicate 2-ml portions were each counted twice. A preset count of 900,000 counts was used in channel A of the counter (the lower energy channel), and the elapsed counting time ranged from 2.76 to 2.80 minutes, with a mean of 2.78 minutes. The calibration curves indicated a tritium counting efficiency of 13.5 percent. Accounting for the several dilutions and the counting efficiency, and converting to a curie basis, the calculations yield directly a total quantity of tritium released to the river of 0.540 curies, or 540 mc. Since this represents four vials of tritiated water as procured, each vial contained 135 mc of tritium as 25 ml of water.

The separate krypton-85 dose consisted of dissolving four kryptonate capsules in a liter bottle in the field laboratory (the exact volume was 1,090 ml), and diluting a 1-ml portion of that solution to 2 liters. Samples of the latter solution were sent to the headquarters laboratory for analysis, and replicate 2-ml portions were prepared and counted, using a preset count of 900,000 counts in channel B of the counter (the higher energy channel). The elapsed counting time ranged from 3.68 to 3.80 minutes, and averaged 3.743 minutes. In addition to the 900,000 counts recorded in channel B, an average of 101,800 counts was recorded in channel A, and the total mean count was therefore 1,001,800 in 3.743 minutes. Use of the counter's standard source with calibration curves indicated a krypton-85 counting efficiency of 58.4 percent. Correcting for the dilutions and converting to a curie base, the total krypton-85 dose was calculated to be 0.226 curies, or 226 mc. This amounted to a dissolved quantity of 56.5 mc per kryptonate capsule, and represented about 60 or 65 mc of krypton-85 in each of the originally undissolved capsules.

The krypton-85 : tritium ratio that resulted from independent analysis of the two tracer doses was therefore $(\frac{226}{540})=0.418$ mc of krypton-85 per mc of tritium.

The mixed dose sample consisted of a 2-ml portion taken in the field from the dose container (exact volume 4,600 ml) and diluted in the field up to 1,090 ml in the 1-liter bottle. Samples of the latter dilution were shipped for analysis, and replicate 2-ml portions were analyzed for their tritium and krypton-85 content in the presence of the dye. A preset count of 900,000 counts was used in channel B of the counter; the elapsed counting period averaged 5.115 minutes, and the mean observed count in channel A was 585,000 counts. Use of the standard source and the calibration curves indicated that 173,000 krypton-85 counts had been recorded in channel A; the total observed krypton-85 count was therefore 1,073,000 counts, and the total tritium count was 412,000 counts in the elapsed time of 5.115 minutes. The krypton-85 counting efficiency was 51.5 percent and the tritium counting efficiency was 8.2 percent. The calculated quantities of tritium and krypton-85 present in the dose container and released to the river were therefore 554 and 231 mc, respectively, and the calculated dose ratio was thus $(\frac{231}{554})=0.418$ mc of krypton-85 per mc of tritium. The agreement with the independently determined tritium and krypton-85 doses was excellent, and the dose ratio of 0.418 was quite firm.

River Sample Calculations.—The radiotracer concentrations in the river samples were much lower than in the dose samples, and the background correction was much more important as a result. The three river water samples taken at and near the peak dye concentration for station number 1 will serve as an example of the calculations involved.

The three river samples for each station were shipped directly to the headquarters laboratory for analysis without dilution. There, three replicate 2-ml portions of each of the three samples for station 1 were prepared for counting, and each vial was counted twice by recycling; this provided a total of six separate counts, each 20 minutes in duration, for each sample, and a total of 18 separate counts for the sampling station, or a total counting time of 6 hours for the station. In addition, six replicate 2-ml portions were prepared for counting from a background river water sample collected at station number 1 well in advance of the dye mass; each of these was also counted twice, for a total background counting period of 4 hours for the station.

The 18 individual observed sample counts in channel A of the counter ranged from 535 to 626 counts, with a mean of 578 counts; the observed channel B counts ranged from 666 to 769 counts and averaged 720 counts. The 20-minute

background counts ranged from 188 to 239 in channel A and averaged 212, whereas in channel B they ranged from 354 to 426 counts and averaged 381. Thus, the net channel A count was (578 − 212) = 366 counts, and the net observed channel B count was (720—381) = 339 counts. The calibration curves indicated that an additional 48 krypton-85 counts had been recorded in channel A, hence the actual net 20-minute krypton-85 count totaled 387 counts, and the actual net tritium count was 318 counts in 20 minutes. The efficiency of krypton-85 counting was 54.9 percent, and the tritium was counted with an efficiency of 11.2 percent. The mean krypton-85 : tritium concentration ratio for station number 1 was therefore

$$\frac{(\frac{387}{0.549})}{(\frac{318}{0.112})} = 0.248,$$

as against the original dose ratio of 0.418.

Because of the low tracer concentrations, the observed concentration ratios were also separately determined for the three individual samples for the station by the same procedures. The three individual sample ratios were 0.248, 0.240, and 0.258, and averaged 0.249, in excellent agreement with the mean of 0.248 obtained by using all 18 results together.

The concentration ratios for all samples and for all tracer releases were calculated according to the foregoing procedures. The ratios for the individual river samples compared very well with the mean ratio obtained for all samples, with very few exceptions. The comparison of krypton-85 and tritium doses as determined by independent analyses of the separate doses and the mixed dose was also usually very good, but in one case the mixed dose sample for assay was lost.

Calculation of Gas Exchange Coefficients.— The gas exchange coefficients for krypton-85 were customarily obtained by the graphical procedure outlined earlier, as a simple and direct means of analysis. For purposes of showing the calculations, however, the krypton-85 and oxygen exchange coefficients will be determined here analytically for the above example.

The elapsed time between the time of dose release (0541 hours) and the time when the peak dye concentration passed station number 1 (1012 hours) was 4.52 hours in the above case. Thus $(\frac{0.248}{0.418}) = 0.594$, whence 59.4 percent of the quantity of krypton-85 originally released was still present as dissolved gas in the water when the dye peak reached station number 1, and 40.6 percent of the original quantity dosed had been lost to the atmosphere in the subreach between the dosing point and station number 1. Using the expression given earlier for the necessary calculations:

$$0.594 = e^{-0.1883\ K_{Kr}}$$

since 4.52 hours is 0.1883 days. Solving this equation yields $K_{Kr} = 2.77$/day for the subreach; dividing by the krypton : oxygen ratio of 0.83 yields $K_{Ox} = 3.34$/day, and converting this result to the common logarithm base we obtain $(k_2)_{Ox} = 1.45$/day. This is the reaeration capacity coefficient for the subreach under consideration at the prevailing temperature and river flow, and is the result that will later be compared to the predictions of the O'Conner-Dobbins and the Churchill reaeration models.

One further question considered at the time of the Little Miami River developmental studies was the degree of error that might be introduced by the use of stream samples collected at times slightly different from the exact time of passage of the dye peak. In other words, would there be a significant difference between the observed krypton-85 : tritium concentration ratios from a sample at the peak dye concentration and another taken, say, 5 to 10 minutes earlier or later? It was found in the Little Miami studies that the observed ratio was not affected to any detectable extent if the time of flow in the reach was long relative to the difference in time between collection of the sample and passage of the dye peak at a sampling station. The same result was found in the Jackson River studies. For example, the time of flow between the dosing point and station number 1 was 4.52 hours, as noted above for Dump No. 14; one of the three river samples analyzed was collected at the dye peak and the other two were collected within 6 minutes on either side of the dye peak time of flow. No significant difference in the observed concentration ratios for the three samples was found, and none should be expected.

The capacity of the liquid scintillation counter proved to be the main limiting factor in the rate with which the Jackson River field operations could be conducted. The system of replication and recycling of the counting vials for all of the samples from one tracer release kept the counter in continuous operation for a period of 30 to 36 hours. This barely allowed sufficient time for re-

ceiving the samples, preparing them for counting and tabulating the results, if the tracer releases were to be scheduled about 48 hours apart. Thus, even had more personnel been available for the field and laboratory operations, the tracer releases could not have been scheduled closer together without sacrificing the excellent counting statistics and the highly important system of verifying results.

JACKSON RIVER STUDIES

The Jackson River originates in the mountains of West Virginia and Virginia and flows southeast through Covington and Clifton Forge, Va.; below Clifton Forge it joins the Cowpasture River and becomes the James, to flow past Lynchburg to the ocean at Norfolk, Va. The drainage area above Covington is about 440 square miles, and the nearest upstream gaging station is located at Falling Springs, Va., about 18 miles above Covington. Two small tributaries in the vicinity of Covington (Dunlap Creek, about one-half mile below the papermill, and Pott's Creek, about 5 miles below the papermill) add small increments of flow. The Jackson below Covington is relatively wide and shallow, and is characterized by a series of riffles and natural pools, and an associated considerable range of velocities and depths. Its reaeration capacity is substantial. Severe droughts occur, and at such times all of the main flow is withdrawn and used at the West Virginia Pulp & Paper Co. paper mill located in Covington, and the downstream flow is then entirely mill treatment plant effluent.[27]

Wastes from the papermill constitute the major B.O.D. load to the river, even after 80 to 90 percent B.O.D. removal in an activated sludge treatment plant at the mill, and at times of low stream flow the stream reaeration capacity is not sufficient to prevent serious or complete depletion of the stream's oxygen resources. Thus, as a further measure designed to improve the situation, the West Virginia Pulp & Paper Co. operates two pairs of mechanical aerators in the stream itself at locations below the mill. It has been noted that mechanical aeration of the main stream flow is accompanied by accelerated stream deoxygenation rates downstream from the aeration units.[27]

During the 2-week period of the reaeration tracer studies reported here, the combined flow of the Jackson at Falling Springs and of Dunlap Creek ranged between 75 and 90 c.f.s., a moderate drought condition. Also, immediately prior to the beginning of the reaeration studies, the secondary effluent treatment units at the paper mill failed, and the paper mill waste treatment plant operated essentially as a primary treatment plant for several days. Arrangements had been made earlier for the downstream mechanical aerators to remain idle during the survey period, in order not to confuse the results of both the stream oxygen balance studies and the tracer studies. As a result of the above combination of factors, the stream oxygen resources were completely exhausted below the papermill for several days, and zero D.O.'s were observed in a reach several miles long. The recovery zone then began downstream from Pott's Creek. The secondary treatment units at the papermill were back in operation within a few days, and the stream D.O.'s improved thereafter, although the reach below the mill was still characterized by quite low D.O.'s.

During the period immediately prior to the tracer studies, the Jackson River was cross-sectioned at intervals of about 1,000 feet between Covington and Clifton Forge by Civil Engineering staff personnel of the Virginia Military Institute for the Chesapeake Project of the Federal Water Pollution Control Administration (FWPCA). The same personnel conducted an intensive oxygen balance survey of this section of the river throughout the first week of the reaeration tracer studies. The FWPCA's Chesapeake Project also supplied four field personnel to man the fluorometers used during the tracer studies.

Dosing Pattern

Figure 15 is a general map of the portion of the Jackson River between Covington and Clifton and Clifton Forge, showing relevant features and the locations of the sampling and dosing stations used in the tracer studies. Several of these stations were also sampling stations for the concurrent oxygen balance studies. The 16 tracer study stations were usually a little more than a mile apart, the average subreach length being 1.13 miles, and the range of lengths being 0.75 to 1.58 miles. The 15 subreaches covered a distance of 17.0 miles and did not quite reach Clifton Forge, but did fully include both the critical and the recovery zones of the prevailing oxygen sag.

Table XI shows the dosing pattern that was used in the tracer studies. As indicated earlier, this pattern of eight separate tracer releases was designed to provide coverage of each of the

N
WESTVACO
MILL
DUNLAP CR
RIVER
COVINGTON
UPPER
AERATORS
JACKSON
RAYON
TERRACE
HERCULES
POWDER CO.
SEWAGE
DISPOSAL PLANT
PARRISH
CRT
LOWER
AERATORS
POTTS CR
US 220 & 60
JACKSON
RIVER
1
2
3
4
5
6
7
8
9

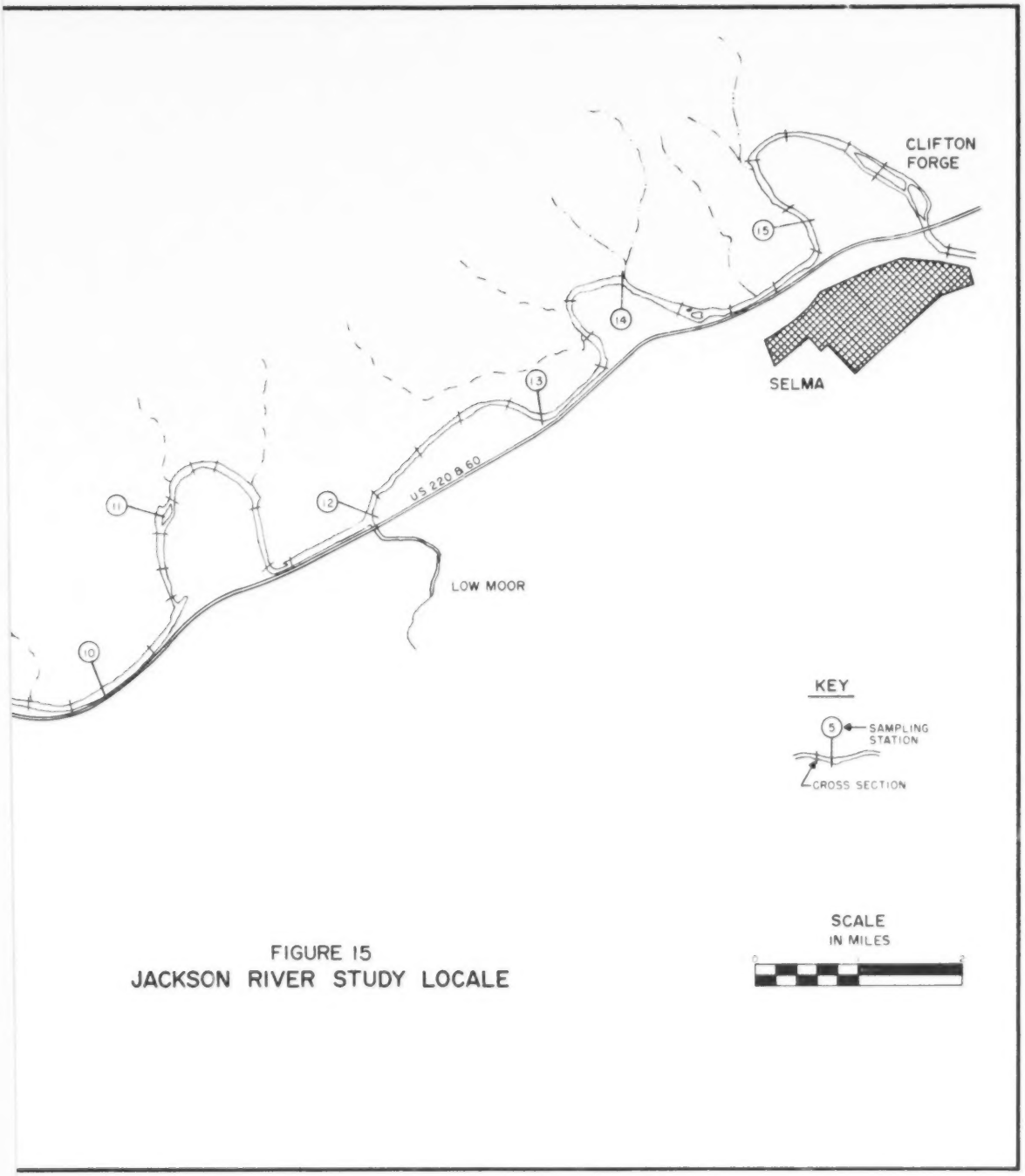

FIGURE 15
JACKSON RIVER STUDY LOCALE

TABLE XI.—Dosing pattern

Dump number	Jackson River sampling station number															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
10	7/11															
	350															
	1088															
11	7/13															
	458															
	273															
12					7/15											
					(450)											
					273											
13					7/17											
					231											
					542											
14								7/19								
								231								
								554								
15									7/21							
									321							
									1088							
16											7/23					
											318					
											1042					
17												7/25				
												321				
												1108				

Key: 7/19—Dump No. 14 released on 7/19/66.
231—231 mc of krypton-85 released.
554—554 mc of tritium released.

subreaches at least twice, as a general means of testing the reproducibility of the reaeration rate coefficients determined by the tracer method. The tracer doses were released every 2 days in the early morning. As may be seen from Table XI, the quantities of tracer doses were varied substantially, the krypton-85 dose ranging from 231 to 458 mc, and the tritium dose from 273 to 1108 mc. The krypton-85 : tritium dose ratio was also varied, and ranged from 0.29 to 1.67 mc of krypton-85 per mc of tritium. This variability of dose and dose ratio was only partly by design, part also being due to the inaccuracy of the radioassays initially available from the suppliers. Only one of the individual doses was still questionable after analysis of all of the dose samples, namely the quantity of krypton-85 released in Dump No. 12. In that case, the mixed dose analysis and the separate krypton-85 dose analysis both yielded erratic results, and the krypton-85 dose was estimated primarily on the basis that the same number of kryptonate capsules was used in Dump No. 11, and all handling procedures were also the same.

Summing the individual doses shown in table XI, a total of 2.68 curies of krypton-85 and 5.97 curies of tritium was released to the river in the studies. The average dose used was 335 mc of krypton-85 and 746 mc of tritium.

Times of Flow

The individual subreach times of flow are presented in Table XII, and represent the arrivals of the peak dye concentrations at successive sampling stations. Figure 16 shows the four dye concentration curves that were observed for Dump No. 14 at stations 1 through 4. The four curves have all been started at a common origin to show the relative dilution and dispersion that took place in the 5.03 miles involved. These curves are typical of the quality of data that was obtained. In no case was there difficulty in closely determining the time of arrival of the peak dye concentration. In one case (Dump No. 10) the dye curve for the first sampling station displayed somewhat more irregularity of shape and smoothness than in other cases, due undoubtedly to some lack of smooth-

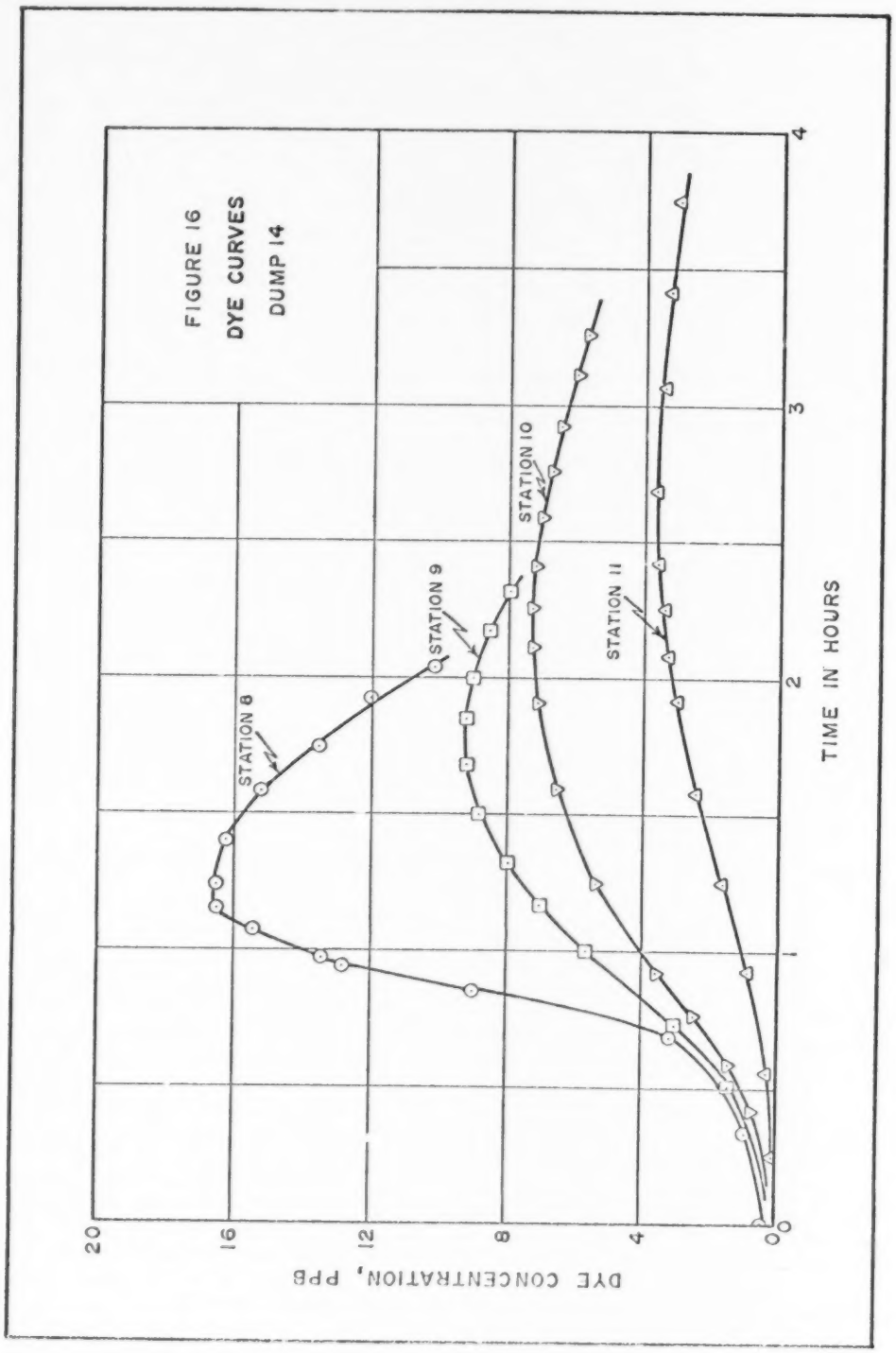
FIGURE 16
DYE CURVES
DUMP 14
STATION 8
STATION 9
STATION 10
STATION 11
DYE CONCENTRATION, PPB
TIME IN HOURS
0
4
8
12
16
20
1
2
3
4

TABLE XII.—Times of passage

Dump number	Time of flow, hours, between stations															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
10	1.65	4.32	6.70	4.42												
11	1.85	4.73	6.20	4.60												
12					2.92	4.45	3.38	4.58	4.48							
13					3.03	4.60	3.17	6.08								
14								4.52	4.38	2.75	2.78					
15									3.90	2.63	2.78	5.05				
16											2.43	4.88	2.65	3.62		
17												4.78	3.12	3.53	3.73	
Mean total time.	1.75	6.28	12.7	17.2	20.2	24.7	28.0	32.6	* 36.8	39.5	42.2	47.1	50.0	53.5	57.2	

* The value 6.08 hours from Dump No. 13 eliminated.

TABLE XIII.—Observed reaeration rate coefficients *

Dump number	$(k_2)_{ox}$, per day, between stations															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
10	1.91	1.33	1.39	(0.89)												
11	1.74	1.71	1.09	0.75												
12					1.71	1.07	1.52	1.51								
13					2.29	1.10	1.58	1.38								
14								1.45	1.45	3.60	(1.17)					
15									1.40	4.00	1.30	1.57				
16											1.45	1.59	3.10	1.33		
17												1.89	2.18	1.88	1.10	
Mean	1.82	1.52	1.24	0.82	2.00	1.08	1.55	1.45	1.42	3.80	1.31	1.68	2.64	1.60	(1.10)	
±%	4.8	12.5	12.1	8.5	14.5	1.4	1.9	3.0	1.8	5.3	7.4	8.2	17.4	17.5		

* At river temperatures ranging from 35° C. to 25° C.

ness in dosing, but this was not of sufficient degree to affect the results.

The reproducibility of subreach flow times in successive tracer releases was excellent, with few exceptions, especially in view of the fact that the tracer releases were two days apart. The 6.08 hours observed for Dump No. 13 in subreach (78) disagrees substantially with the other two observed values (4.52 and 4.58 hours), and the exact reason for this discrepancy is not known. This and other lesser differences could have been the result of one or more of several causes, including transitory variability of the main river flow in the reach and its tributaries, local rain showers (which did occur several times), and variability of the influent and effluent flows at the paper mill.

From figures in Table XII, the cumulative mean time of flow through the entire reach of 16 stations was 57.2 hours, or 2.38 days.

Observed Reaeration Rate Coefficients

Table XIII presents the reaeration rate coefficients, $(k_2)_{ox}$, determined by the Jackson River studies. As may be seen, 32 individual subreach values of the reaeration rate coefficient were evaluated, with three subreaches being covered three times, 11 subreaches covered twice, and one subreach, the last, having only a single determination. The values reported in Table XIII are those reflecting the actual river temperatures encountered, and have not been corrected for temperature. The temperature ranged from 35° C. immediately below the papermill progressively downward to 25° C., which was a steady value for the last several miles during the second survey week. The mean subreach river temperatures that were associated with the individual tracer releases are shown below in Table XV.

Figure 17 shows on semilog scales the observed concentration ratios for Dump No. 14, as an ex-

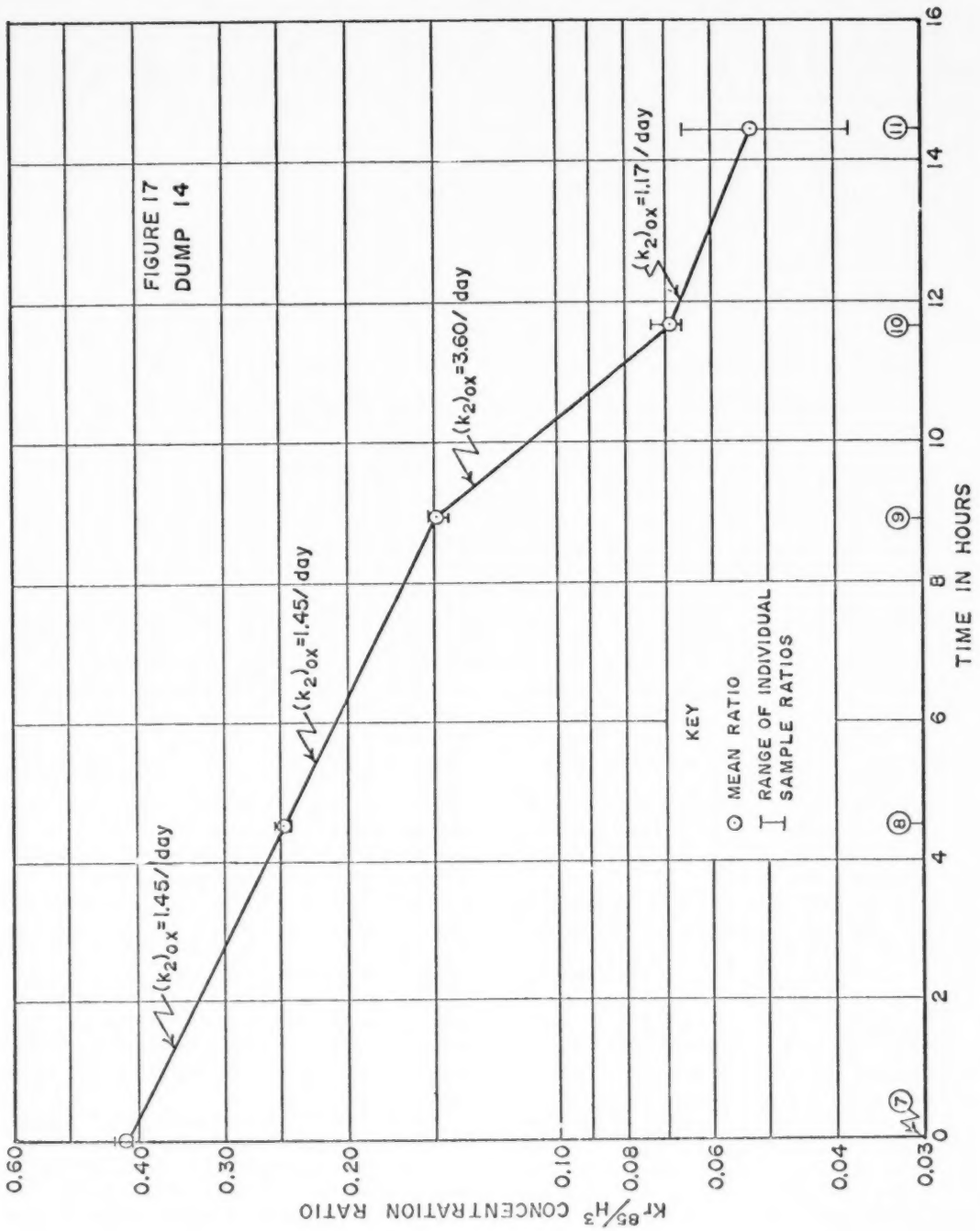
FIGURE 17
DUMP 14
$(k_2)_{ox}$=1.45/day
$(k_2)_{ox}$=1.45/day
$(k_2)_{ox}$=3.60/day
$(k_2)_{ox}$=1.17/day
KEY
MEAN RATIO
RANGE OF INDIVIDUAL SAMPLE RATIOS
Kr^{85}/H^3 CONCENTRATION RATIO
0.60
0.40
0.30
0.20
0.10
0.08
0.06
0.04
0.03
0
2
4
6
8
10
12
14
16
TIME IN HOURS

TABLE XIV. Observed reaeration rate coefficients*
[25° C.]

Dump number	$(k_2)_{ox}$, per day															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
10	1.54	1.14	1.25	(0.80)												
11	1.40	1.47	0.98	0.67												
12					1.60	0.98	1.39	1.38								
13					2.15	1.03	1.45	1.26								
14								1.42	1.45	3.60	(1.16)					
15									1.43	4.00	1.27	1.50				
16											1.45	1.59	3.03	1.30		
17												1.89	2.23	1.88	1.07	
Mean	1.47	1.30	1.12	0.74	1.88	1.01	1.42	1.35	1.44	3.80	1.29	1.66	2.63	1.59	(1.07)	
±%	4.8	12.6	12.0	8.8	14.6	2.5	2.1	4.7	0.7	5.3	8.0	9.3	15.2	18.2		

*Corrected to 25° C. by the use of $\theta = 1.022/^\circ$ C.

ample of the observed results and the derived values of $(k_2)_{ox}$. The slopes of the lines between the individual sampling stations reflect the $(k_2)_{KR}$, and have been corrected by the factor 0.83 to derive the values of $(k_2)_{ox}$ that are shown. In the case of Dump No. 14, the dose ratio was 0.418. For each sampling station the mean observed concentration ratio and the range of individual sample ratios are shown. (The mean ratio is obtained by summing all observed counts for the three samples and dividing by the total number of times counted, as this procedure is statistically more appropriate than taking the mean of the three individual sample ratios.) In this case, the three individual samples for stations 10 and 11 were recycled three times in the liquid scintillation counter instead of twice to improve the counting statistics, as quite low krypton-85 counts were expected. Thus, for stations 10 and 11 there was available a total of 27 individual sample counts of 20-minute duration each.

As may be seen from Figure 17, the range of concentration ratios observed for the three individual samples was quite narrow at stations 7, 8, 9 and 10, and the mean ratios were quite firm figures. The range of observed individual sample ratios at station 11 was considerably larger, due to the low quantity of krypton-85 remaining in solution at station 11 (only 12.7 percent of the amount originally dosed was still present at station 11), and the resulting small difference between the total count rate and the background count rate in channel B of the counter. The mean concentration ratio observed at station 11 is thus a more questionable figure, even though it represents 540 minutes of counting time. However, reference to Table XIII indicates that the derived value of $(k_2)_{ox}$ for the subreach (1011) was quite comparable to the values obtained from Dumps No. 15 and 16, where no such counting problem was encountered, and thus that the use of the mean concentration ratio observed for station 11 in Dump No. 14 produced a close result due to the long counting times used.

The deviation of the individual sample ratios from the mean value for station 11 in Dump No. 14 was one of the two most pronounced cases found, the other being the observed results at station 4 for Dump No. 10; no other case of serious doubt regarding the accuracy of the mean observed concentration ratio was encountered. The derived values of $(k_2)_{ox}$ for reach (34) for Dump No. 10 and for reach (1011) for Dump No. 14 are bracketed in Tables XIII and XIV to indicate that they are somewhat more doubtful than the other values shown.

Referring to Table XIII, the range of observed individual subreach reaeration coefficients was from 0.75 to 4.00 per day. The mean value for each subreach is also shown, together with the average deviation of the individual results expressed as a percent of the mean reaeration coefficient. Thus, for instance, in subreach (01) the mean reaeration coefficient was 1.82 per day, and the average deviation of the two individual values was 0.085 per day, or 4.8 percent of the mean value of 1.82 per day.

In order to put all the observed values of $(k_2)_{ox}$ on a comparable basis, and for purposes of later comparison to values obtained from the predictive models, all of the observed reaeration coefficients have been converted to a common temperature of 25° C., and these results are shown in Table XIV. The temperature corrections were made on the

basis of the value of $\theta = 1.022$ per degree centigrade derived earlier from the development of the basic reaeration equation.

Reproducibility.—Reference to Tables XIII and XIV indicates that the reproducibility of the individual observed values of the reaeration coefficient in the 15 subreaches was excellent, the worst case involving a deviation about the mean value of 18 percent. In nine cases out of the 14 for which at least two results are available, the average deviation of the individually observed values of $(k_2)_{0x}$ was less than 10 percent of the mean value, and in six cases the average deviation of the individual results was less than 5 percent of the mean result. Bearing in mind that the tracer releases were at least 2 days apart (4 days apart where three values of the reaeration coefficient are shown), that both the individual tracer doses and the dose ratios were varied substantially in the studies, and that some local rainfall occurred as well as some variation in river flows, this degree of reproducibility of results is highly satisfactory. It is regarded as excellent general experimental verification of the field and laboratory procedures and of the approach to the problem.

Observed Versus Predicted Reaeration Coefficients

The observed values of the reaeration coefficient may now be compared to the values that are predicted by the O'Connor-Dobbins model [5] and by the model provided by Churchill, Elmore and Buckingham.[13] For this purpose, Table XV gives the physical characteristics of the 15 subreaches. The temperature corrections used here for the two predictive models were the values preferred by the individual authors of the models.

Referring to Table XV, each subreach length was scaled from large scale USGS quadrangle maps in order to obtain the subreach lengths in miles. The mean depths for the subreaches were obtained from the cross-sections provided by the Chesapeake Project at intervals of about 1,000 feet, an average of six or seven cross-sections being available for each subreach; in each case, the mean depth for the subreach was obtained by averaging the individual values of cross-sectional area divided by stream width. The mean depths for the 93 individual cross-sections varied from a minimum of 0.58 foot to a maximum of 5.30 feet; 15 percent were less than 1.0 foot, 55 percent were less than 2.0 feet, 76 percent were less than 3.0 feet, and 94 percent were less than 4.0 feet. The mean velocities for the subreaches were obtained by dividing the length of the subreach by the mean time of flow obtained from the dye curves, with appropriate dimensional conversions, as available information regarding stream flow at the 16 individual stream sampling stations was not sufficiently accurate for this purpose, and the main stream flow was not sufficiently steady.

TABLE XV.—Physical characteristics of subreaches

Subreach	Length, mi.	Mean depth, ft.	Mean velocity, ft/sec	Mean temp., ° C.
01	0.757	1.76	0.636	35
12	1.290	1.94	0.419	32
23	1.579	2.09	0.359	30
34	1.408	3.11	0.458	30
45	1.157	1.67	0.570	28
56	1.069	2.36	0.346	29
67	0.746	1.99	0.333	29
78	1.477	2.26	0.436	29
89	0.826	2.83	0.286	25
910	1.034	2.30	0.563	25
1011	0.955	1.95	0.529	25
1112	1.472	2.42	0.441	25
1213	1.053	2.13	0.539	25
1314	1.038	2.06	0.425	25
1415	1.163	1.66	0.457	25

Table XVI presents the comparison of ob-

TABLE XVI.—Comparison of observed and predicted reaeration coefficients
[25° C.]

Subreach	$(k_2)_{0x}$, per day		
	Mean observed	O'Connor-Dobbins *	Churchill et al.**
01	1.47	2.04	1.41
12	1.30	1.43	0.80
23	1.12	1.18	0.61
34	0.74	0.74	0.41
45	1.88	2.09	1.40
56	1.01	0.97	0.49
67	1.42	1.23	0.62
78	1.35	1.16	0.64
89	1.44	0.68	0.31
910	3.80	1.29	0.81
1011	1.29	1.60	1.00
1112	1.66	1.06	0.58
1213	2.63	1.41	0.88
1314	1.59	1.32	0.74
1415	1.07 ***	1.89	1.13

* $(k_2)25° C. = 5.97 \frac{V^{0.50}}{H^{1.50}}$

** $(k_2)25° C. = 5.66 \frac{V^{0.960}}{H^{1.672}}$

*** One observation.

served and predicted values of the reaeration coefficient, k_2, at 25° C. The observed values are the means taken from Table XIV, and the predicted values have been calculated according to the equations shown with Table XVI and using the velocities and depths given in Table XV. As may be seen in Table XVI, eight of the observed reaeration coefficients are larger than both predicted values, six lie between the two predicted results, and one is slightly less than the lower predicted value. The observed reaeration coefficient varied from 0.95 to 4.70 times the value predicted by the Churchill model, and from 0.57 to 2.95 times the value predicted by the O'Connor-Dobbins model.

These comparative results must be interpreted with caution, particularly because of the usual distance between stream cross-sections that were available. Thus, although the number of cross-sections available per subreach is certainly adequate for general descriptive purposes and for reasonable estimates of mean subreach cross-sectional area and depth, it may not be adequate for close comparative analysis of the results shown in Table XVI. In other terms, the mean depths given in Table XV and used for Table XVI may not be as accurate or as representative in any individual case as might have been provided by cross-sections observed at closer intervals. Of course, in the ordinary stream survey, the frequency with which stream cross-sections can be determined is limited by available personnel, time and costs, so that the usual six cross-sections per subreach is not at all unacceptable from the standpoint of ordinary practice. However, in a stream of this type it cannot be regarded as adequate for highly accurate computations of mean subreach cross-sectional area, depth and volume.

It should also be noted that the comparison shown in Table XVI represents only one stream of a particular type, namely relatively small and shallow and characterized by a series of numerous riffles and pools and a relatively wide range of velocities through individual cross-sections. Thus, there is no adequate basis for extending the numerical comparisons shown in Table XVI to other types of stream such as rivers that are larger and deep and slow, impounded waters, or tidal estuaries.

With the above reservations in mind, the comparisons presented in Table XVI do permit certain conclusions. First, the tracer method of measuring stream reaeration capacity and the two predictive models all provide results in the same range for a stream of the Jackson River type. The reproducibility of results by the tracer method proved to be excellent, and the degree of agreement between the predicted results and the independent measurements is in general very good. The independent measured values of k_2 thus provide general verification of the predictive models.

Secondly, it is clear from the results shown in Table XVI that the predictive models may err by a factor of three or more in reaches a mile long in streams of this type, at least if the available cross-sections are not considerably closer together than every 1,000 feet. It should also be noted here that Churchill, Elmore and Buckingham called attention to the fact that their model might err on the low side if there was much "white water."

Although it may appear that the predictions of the O'Connor-Dobbins model agree more closely with the observed results than do those provided by the Churchill model, the available quantity of cross-section data is not regarded as sufficient to justify this conclusion. The observed values do tend generally to be higher than the predicted values, and this is not surprising for a stream that contains a substantial number of riffles, as neither model adequately encompasses that situation. The data of Table XVI are too limited in quantity (only one stream) and in quality (frequency of cross-sectioning) to justify any conclusion that one predictive model is better than the other at this time.

It should be noted also that the exponent of the velocity term has a particularly strong effect in creating the differences between predictions from the two models, as the main coefficients and the exponents of the depth terms are not greatly different. The earlier work of Streeter and Phelps [7] with the very similar model

$$k_2 = \frac{c\,V^n}{H^2}$$

showed that the coefficients c and n were both highly variable for different reaches of the Ohio River. Thus it would not be surprising to find in further work that the degree to which observed values of k_2 agree or disagree with either model, or for that matter with the Streeter-Phelps model, is a matter involving the particular type of stream, and either model may provide the better results in one stream or another.

The more important issue involves the degree of error that may be associated with any individual prediction by either model for a specific reach

of a specific stream, as the actual costs of pollution abatement will depend upon specific values of k_2 rather than on the general statistical accuracy of a model. On this point the data of Table XVI provide a definite initial determination for streams of the Jackson River type, the individual subreach predictions differing by as much as a factor of three or more from the measured values. The fact that the largest differences involve low predictions by both models is most probably simply indicative of the especially effective mixing and reaeration that take place in shallow, fast riffle reaches.

Summary

The reaeration capacity of a 17-mile reach of the Jackson River has been determined by the gaseous tracer method. For this purpose, the 17-mile reach was separated into 15 subreaches averaging a little more than a mile in length. The reaeration coefficient, k_2, was determined at least twice for all except one subreach by means of a series of eight separate tracer releases at 2-day intervals. A total of 32 separate subreach values of k_2 were thus determined, three subreaches being covered three times, 11 subreaches being covered twice, and one subreach a single time.

Reproducibility of the derived values of k_2 was excellent. Although the individual tracer doses and the dose ratios were varied substantially, the releases were 2 days apart, and some variability of river flow was encountered, the individual observed values of k_2 were usually within 10 percent of their mean value (nine subreaches out of 14), and the worst case involved individual results that were within 18 percent of the mean value.

The observed values of k_2 were also compared to values predicted by the O'Connor-Dobbins model [5] and the Churchill model,[13] and all results were found to lie within the same range. Eight of the observed values of k_2 were higher than both predicted values, six lay between the two predicted values, and one was slightly less than the lower predicted value. Although these comparisons represent only one stream, relatively small, shallow and characterized by numerous riffles and pools, they show that for streams of this size and type the predictive models provide results that are generally in the correct range. They also demonstrate that the values of k_2 predicted for individual subreaches a mile long may err by a factor of three or more, at least if physical data from stream cross-sectioning are not available at intervals considerably less than every 1,000 feet. The comparisons available do not demonstrate any preference of predictive models, and should not be extended to streams that are deep and slow, to impounded waters, or to tidal estuaries.

These field studies have demonstrated that direct independent evaluation of the reaeration capacity of natural streams by the use of tracers is feasible and provides highly reproducible results. If such studies are conducted in the same reaches at several different flows, an accurate relationship between the reaeration capacity and river flow can be established and should remain valid indefinitely, if the physical and hydraulic characteristics of the reach are not changed substantially by the introduction of channel diversions, dams, etc.

general summary and conclusions

This chapter contains a brief general summary of the studies that have been made and of the conclusions that they appear to justify. For details of the studies and bases of the conclusions, reference to the preceding chapters of the report is necessary.

CHAPTER FIVE

SUMMARY

The ability of a stream to obtain oxygen from the atmosphere is the fundamental process by which the stream is able to purify itself, or to recover its oxygen resources once they have been depleted by bacterial degradation of organic wastes. Accurate knowledge of this reaeration capacity is a necessity for successful pollution control, as it is the necessary basis for accurate evaluation of waste treatment requirements, associated costs, and proposed stream standards. No independent method of accurately evaluating the reaeration capacity has been available, however, primarily because reaeration depends on turbulent mixing and there is no independent means of measuring turbulence in a flowing stream. The available methods for estimating reaeration capacity depend either upon indirect balancing of all oxygen resources and demands, which most often cannot be accomplished accurately, or upon the use of mathematical predictive models whose general validity cannot be proved and for which the associated error of prediction is unknown. Both presently available means of estimating reaeration capacity are therefore inadequate.

This report describes a new technique for accurate and fully independent direct field measurement of stream gas exchange capacity, based upon the simultaneous use of tracers for dispersion and for gas exchange. The preceding sections of the report contain detailed descriptions of the technique, its basis, the supporting laboratory investigations and the full scale field demonstration. This technique makes possible the evaluation of stream reaeration capacity with a degree of accuracy and dependability not heretofore achievable.

Reaeration of turbulent water is a physical process that takes place by the combined effects of molecular diffusion of the gas and physical mixing of the water. The oxygen molecules can enter the water only at the surface, and must subsequently become distributed throughout the fluid medium. In a stagnant fluid, reaeration is very slow, because distribution throughout the fluid volume depends upon molecular diffusion of the dissolved gas and that is a slow process. Mixing of the water brings about continuous replacement of the surface water layer and greatly increases both the net rate of entry of gas molecules at the water surface and the subsequent rate of distribution and diffusion throughout the whole volume. Thus, turbulent mixing greatly increases the reaeration capacity. It is unfortunate that no in-

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dependent means of measuring turbulent mixing is available.

The available predictive models generally represent an attempt to relate reaeration capacity to turbulence, and those in common use take the form [5 7 13]

$$k_2 = \frac{c\,V^n}{H^m}$$

where k_2 is the desired reaeration coefficient, V is the mean channel velocity, H is the mean depth of flow, and c, n and m are constants that are evaluated either empirically or on the basis of a set of assumptions regarding turbulence. It has been impossible thus far to verify such models because it has not been possible independently to evaluate k_2. Thus it is not presently known whether any model of the above form is adequate for predictive purposes, which of the available models might be best, or what the associated errors of prediction amount to.

The field tracer method for evaluating stream reaeration capacity depends upon a series of analogies and the simultaneous use of three tracers, a fluorescent dye, a dispersion tracer (tritium) and a gaseous tracer (krypton-85). The dye provides time of flow and indicates when to sample for the two radioactive tracers. The tritium, present as tritiated water, provides a measure of the total dispersion that has occurred within a river reach. The krypton-85, present in the dissolved state, undergoes the same dispersion, and, additionally, is lost to the atmosphere through turbulent mixing and escape at the water surface. In any reach of stream, the percent of dissolved tracer gas that has been lost is readily and simply evaluated on the basis of the upstream and downstream concentration ratios of krypton-85 and tritium. Methods of analysis for the water concentrations of both radiotracers have been developed and are highly sensitive and accurate, hence the percent loss of tracer gas in a river reach can be quite accurately evaluated.

The relationship between the exchange capabilities of dissolved oxygen and dissolved krypton-85 has been the subject of extensive laboratory investigation. It has thus been established that the gas exchange coefficient of krypton-85 is 83 percent of the exchange coefficient for oxygen, and that this ratio is a constant under a wide variety of conditions of turbulence, temperature, direction of gas transfer, etc. Thus the field-determined values of the gas transfer coefficient for krypton-85 are readily converted to values of k_2, the reaeration coefficient.

The assumptions upon which the tracer method are based are: (1) The tritiated water undergoes only dispersion in the stream, and is not lost from the stream water in any significant amount; (2) the dissolved krypton-85 undergoes the same dispersion as the tritiated water, in addition is lost to the atmosphere, and is not otherwise lost in any significant amount; (3) the ratio of gas transfer coefficients for dissolved krypton-85 and oxygen of 0.83 is not significantly affected by temperature, turbulence, or the presence of usual water pollutants, in the range of interest. The evidence in support of the validity of these assumptions is presented in the preceding text of this report. No assumptions are made as to the uniformity of the stream channel or of turbulent mixing, nor are assumptions as to the frequency of mixing, mixing length, or the rate of surface replacement required. Although results are expressed as values of k_2, they are understood to be average values for the subreach, and no assumption that reaeration took place as a single first order process in the stream is necessary.

Following the necessary laboratory investigations, the field tracer method for reaeration capacity was demonstrated in full scale field studies of gas exchange in the Jackson River, between Covington and Clifton Forge, Va. A total of eight separate tracer releases was made, involving totals of 2.68 and 5.97 curies of krypton-85 and tritium, respectively, and a total of 32 separate determinations of k_2 were made in 15 subreaches of a 17-mile stretch of the river. Each subreach, averaging a little over a mile in length, was covered at least twice by separate tracer releases. Reproducibility of the k_2 values thus determined proved to be excellent. Comparison of the observed values of k_2 with those predicted by two of the available predictive models demonstrated that the range of predictions was in general good, but that any individual subreach prediction might err by a factor of three or more. These field studies demonstrated the practical feasibility of direct and independent evaluation of the reaeration capacity of natural streams by the tracer method.

CONCLUSIONS

The following conclusions have been reached as a result of the studies reported in detail in preceding sections of this report:

(1) The relative gas exchange capability of krypton-85 and oxygen, measured as the ratio of their respective reaction rate coefficients, is 0.83, with a standard deviation of 0.04, the transfer of krypton-85 being the slower process.

(2) The above ratio of k_2 values of 0.83 is not significantly affected or changed by temperature in the range of 10° C to 30° C., by the degree of turbulent mixing in the range studied, by the direction in which the gases are transferring, or by the presence or absence of a broken water surface; the presence of the dissolved solids in a natural ground water and the presence of ABS in two experiments had no significant effect on the ratio. Although the presence of water pollutants may affect individual values of k_2 and of the saturation limit for dissolved oxygen, there is no reason to expect pollutant concentrations in the usual range of interest to significantly affect the ratio.

(3) It has been shown that for the gases studied the ratio of exchange coefficients of any two gases is equal to the inverse ratio of the molecular diameters of the two gases. The gases studied included hydrogen, helium, nitrogen, oxygen, carbon dioxide, krypton (both radioactive and stable) and radon.

(4) It has been clearly demonstrated that Graham's Law, which expresses the relative diffusion rates of two gases in terms of their molecular weights, is not applicable to gas transfer in turbulent water systems at ordinary pressures.

(5) It has been shown that the available data on the diffusivity of gases in water supports, as well as can be expected, the inverse relationship between diffusivity and molecular diameter that can be predicted from consideration of Fick's Law and Einstein's law of diffusion. This implies further that the gas transfer coefficient, K_2, is directly proportional to the diffusivity. Unfortunately, the available data on the diffusivity of gases in water is quite limited and, for the very light gases, confusing; hence, this relationship cannot be conclusively tested.

(6) Analysis of the kinetics of gas transfer in a mixed water system has shown that the volumetric gas transfer coefficient, K_2, is directly proportional to a constant, b, that reflects the ability of the dissolved gas molecules to escape from the water surface, to the thickness, h, of the interfacial surface water layer from which dissolved gas molecules can directly escape, to the number of surfaces exposed per unit time, n, and to the surface area of contact, A, and is inversely proportial to the volume of fluid, V.

(7) From the analysis referred to in (6) above, it has also been shown that the temperature coefficient, θ, that is commonly used to relate values of k_2 at different water temperatures, has the numerical value of 1.022/degree Centigrade, $\pm$0.003. This is in excellent agreement with Churchill's recently observed value of 1.024.[13]

(8) The field studies of reaeration of the Jackson River have demonstrated that independent direct field evaluation of stream reaeration capacity by the use of tracers is feasible and practical, and that the results that are obtained are highly reproducible.

(9) The field tracer studies of reaeration capacity of the 17-mile stretch of the Jackson River have shown that both the O'Connor-Dobbins predictive model and the predictive model of Churchill, Elmore and Buckingham provide predictions of k_2 that are in the general range of the observed values for streams of this type.

(10) It has also been shown that for shallow streams like the Jackson River, the predictive models for k_2 referred to above may err by a factor of three or more in predicting the reaeration capacity of subreaches a mile long, at least if the predictions are based upon cross-sections that are not considerably closer together than every 1,000 feet.

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